

N 70 41981

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SURFACE OF TD-NiCr UNDER OXIDIZING CONDITIONS**

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August 1970

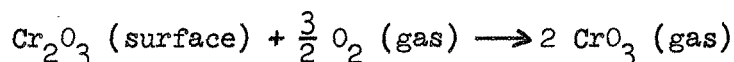
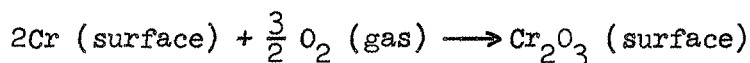
VAPORIZATION OF CHROMIUM OXIDES FROM THE SURFACE  
OF TD-NiCr UNDER OXIDIZING CONDITIONS

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SUMMARY

Thermodynamic calculations and experimental mass spectrometric studies have been made in an effort to elucidate the mode and rate of oxidative vaporization of the thoria-dispersed nickel-20 percent chromium alloy. With thermodynamic data from the literature, vapor pressures for  $\text{CrO}_3(\text{g})$ ,  $\text{CrO}_2(\text{g})$ ,  $\text{CrO}(\text{g})$  and  $\text{Cr}(\text{g})$  were calculated for the equilibrium vaporization of  $\text{Cr}_2\text{O}_3(\text{s})$  over the temperature range from 900 to 1800° K at oxygen pressures from 1 to  $10^{-12}$  atmospheres. The oxidative vaporization for the alloy was characterized by the chemical reactions



and others involving  $\text{CrO}_2(\text{g})$ ,  $\text{CrO}(\text{g})$ , and  $\text{Cr}(\text{g})$  which are volatiles of lesser importance.

The rate of weight loss of Cr from unit surface area per second was calculated as a function of temperature and oxygen pressure and the results are presented graphically in figure 17. Methods of making other calculations for engineering applications are also given.

The enhanced volatility of  $\text{Cr}_2\text{O}_3(\text{s})$  in the presence of water vapor was considered. Calculation of the vapor pressures of  $\text{CrO}_2(\text{OH})(\text{gas})$  were made as a function of temperature, oxygen pressure and water vapor pressure. The results of these calculations are presented in graphical form.

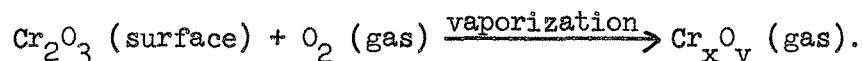
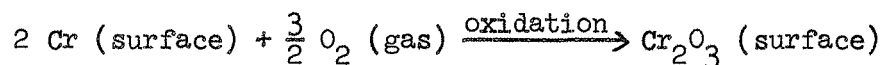
Mass spectrometric studies were conducted and the results indicate that  $\text{CrO}_3(\text{g})$  and  $\text{CrO}_2(\text{g})$  are the important vaporization products in the oxidative vaporization of the TD-NiCr alloy. The experimental results provide verification of the thermodynamic calculations.

## I. INTRODUCTION

TD-NiCr (2 percent thoria-dispersed nickel-20 percent chromium alloy) is being considered for large scale use at elevated temperatures under oxidizing conditions. It is a prime candidate for use as the skin of the space shuttle and in certain turbine engine applications. Thus a thorough knowledge of the corrosive oxidation behavior of the material at moderate oxygen pressures (0.1 to 100 torr) and high temperatures (800 to 1200° C) is important.

The major mechanism of corrosion of TD-NiCr is believed to be the oxidation of Cr at the surface and subsequent vaporization of chromium oxides from the oxidized surface. Extensive studies have been made of the oxidation of the NiCr alloys with particular emphasis on the kinetics of formation, identification, and morphology of the oxide phases (ref. 1). However, the vaporization behavior has been largely ignored. Although in the early stages of oxidation, small amounts of NiO and NiCr<sub>2</sub>O<sub>4</sub> are formed on the surface, it has been shown that, with alloys of greater than 5 weight percent Cr, Cr<sub>2</sub>O<sub>3</sub> is the major phase present on the surface of the material (ref. 1). Equilibrium thermodynamic calculations demonstrate that Cr<sub>2</sub>O<sub>3</sub> is the stable oxide in equilibrium in the Ni-Cr-O system even at low Cr activities (ref. 1).

At moderate temperatures, the bulk Ni and Cr below the surface are protected by the Cr<sub>2</sub>O<sub>3</sub> layer. However, in the temperature range of interest, the vapor pressure of Cr<sub>2</sub>O<sub>3</sub> in the presence of oxygen might be high enough to cause appreciable mass loss. The overall mode of oxidative vaporization of TD-NiCr may be illustrated by the following set of reactions:



As an aid to the understanding of the oxidative vaporization of Cr<sub>2</sub>O<sub>3</sub>(s) under various partial pressures of oxygen, it is necessary to know the composition of the vapor phase. Experimental determinations of the vapor composition and vaporization rate at high velocities (up to Mach 12) and oxygen pressures (0.1 to 100 torr) are difficult and expensive to carry out. Furthermore, the standard types of static furnace tests do not provide the vapor composition data and may give misleading and, at best, not easily interpretable results (ref. 2). Therefore, thermodynamic calculations of vapor composition and an experimental

verification should be useful in establishing definitive experiments necessary to test satisfactorily and reliably the oxidation resistance of TD-NiCr.

In part II of this report we use the thermodynamic data for the Cr-O system from the literature to calculate the equilibrium composition of the vapor phase above  $\text{Cr}_2\text{O}_3(\text{s})$  at various temperatures and under various oxygen partial pressures. For certain applications the action of water vapor on the oxidative vaporization of TD-NiCr is also of interest. Therefore, the calculations were also made using some recent data on the reaction of  $\text{H}_2\text{O}(\text{g})$  and  $\text{O}_2(\text{g})$  with  $\text{Cr}_2\text{O}_3(\text{s})$  to demonstrate the effect of water on the vaporization of TD-NiCr.

In part III of this report are presented the results of our attempts to verify experimentally the results of the calculations; a simple mass spectrometric investigation was made of the vaporization of TD-NiCr samples.

## II. CALCULATION OF VAPOR COMPOSITION

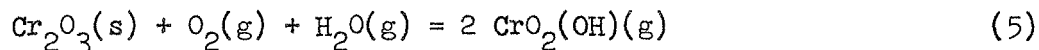
### Purpose

To describe quantitatively the equilibrium mode of vaporization of  $\text{Cr}_2\text{O}_3(\text{s})$  in various oxygen ( $\text{O}_2$ ) and water ( $\text{H}_2\text{O}$ ) vapor atmospheres, it is desirable to know the partial pressures of the vapor species as a function of temperature and  $\text{O}_2(\text{g})$  and/or  $\text{H}_2\text{O}(\text{g})$  pressure. A convenient method for the presentation of the pressure information is the use of thermochemical diagrams of the type described by Jansson and Gulbransen (ref. 3). The diagrams show the vapor pressures of the various gas phase components of the system as a function of oxygen pressure and temperature.

### Vapor Species in the Cr-O-H System

Grimely, Burns, and Inghram have shown that  $\text{CrO}(\text{g})$ ,  $\text{CrO}_2(\text{g})$ , and  $\text{CrO}_3(\text{g})$  along with  $\text{Cr}(\text{g})$  and  $\text{O}_2(\text{g})$  are the major vaporization products in the Cr-O system at high temperatures (ref. 4). McDonald and Margrave have reported the complex polymeric oxide molecules  $\text{Cr}_3\text{O}_9(\text{g})$ ,  $\text{Cr}_4\text{O}_{12}(\text{g})$ , and  $\text{Cr}_5\text{O}_{15}(\text{g})$  over  $\text{Cr}_2\text{O}_3(\text{s})$  at low temperatures (ref. 5), but the thermodynamic circumstances indicate that these species are unimportant in the temperature range under consideration in the present study. Several investigations (ref. 7 and references cited therein) have indicated that the volatility of  $\text{Cr}_2\text{O}_3(\text{s})$  in oxidizing atmospheres is enhanced by the presence of water vapor. Kim and Belton (ref. 7) have attributed the phenomenon to the formation of  $\text{CrO}_2(\text{OH})(\text{g})$ .

Over the temperature range (900 to 1800° K) and  $O_2(g)$  pressure range ( $10^{-12}$ -1 atm) of interest in the present study calculations show that  $Cr_2O_3(s)$  is the stable solid phase in the Cr-O system; no Cr(s) will exist at equilibrium. Therefore, as a starting point for the calculations of the partial pressures of the various Cr-O-H species in the presence of  $O_2(g)$  and  $H_2O(g)$ , the following chemical reactions were considered:



#### Partial Pressures of Vaporizing Species

The vapor pressures of the various Cr-O-H vapor species were calculated by the use of reactions (1) to (5) and pertinent thermochemical relations. For any chemical reaction the equilibrium constant, K, is the ratio of the product of the activities of the products to those of the reactants. Thus the equilibrium constants for reactions (1) to (5) are given as:

$$K_{(1)} = P_{Cr(g)}^2 \cdot P_{O_2(g)}^{3/2} \cdot a_{Cr_2O_3(s)}^{-1} \quad (1A)$$

$$K_{(2)} = P_{CrO(g)}^2 \cdot P_{O_2(g)}^{1/2} \cdot a_{Cr_2O_3(s)}^{-1} \quad (2A)$$

$$K_{(3)} = P_{CrO_2(g)}^2 \cdot P_{O_2(g)}^{-1/2} \cdot a_{Cr_2O_3(s)}^{-1} \quad (3A)$$

$$K_{(4)} = P_{CrO_3(g)}^2 \cdot P_{O_2(g)}^{-3/2} \cdot a_{Cr_2O_3(s)}^{-1} \quad (4A)$$

$$K_{(5)} = P_{\text{CrO}_2(\text{OH})(\text{g})}^2 \cdot P_{\text{O}_2(\text{g})}^{-1} \cdot P_{\text{H}_2\text{O}(\text{g})}^{-1} \cdot a_{\text{Cr}_2\text{O}_3(\text{s})}^{-1} \quad (5A)$$

In all of the calculations we assumed that the activity (a) of  $\text{Cr}_2\text{O}_3(\text{s})$  was one. Therefore equations (1A) to (5A) can be written in an alternate form:

$$\log K_{(1)} = 2 \log P_{\text{Cr}(\text{g})} + \frac{3}{2} \log P_{\text{O}_2(\text{g})} \quad (1B)$$

$$\log K_{(2)} = 2 \log P_{\text{CrO}(\text{g})} + \frac{1}{2} \log P_{\text{O}_2(\text{g})} \quad (2B)$$

$$\log K_{(3)} = 2 \log P_{\text{CrO}_2(\text{g})} - \frac{1}{2} \log P_{\text{O}_2(\text{g})} \quad (3B)$$

$$\log K_{(4)} = 2 \log P_{\text{CrO}_3(\text{g})} - \frac{3}{2} \log P_{\text{O}_2(\text{g})} \quad (4B)$$

$$\log K_{(5)} = 2 \log P_{\text{CrO}_2(\text{OH})(\text{g})} - \log P_{\text{O}_2(\text{g})} - \log P_{\text{H}_2\text{O}(\text{g})} \quad (5B)$$

For any chemical reaction,  $\log K_r = \Sigma \log K_{p,\text{products}} - \Sigma \log K_{p,\text{reactants}}$ , where  $K_p$  is the equilibrium constant for the formation  $p$ , reaction of the various constituents from pure elements in their standard states. Now  $\log K_r$  for reactions (1) to (5) can be set up in terms of the  $\log K_p$  terms for the various components:

$$\log K_{(1)} = 2 \log K_{\text{Cr}(\text{g})} + \frac{3}{2} \log K_{\text{O}_2(\text{g})} - \log K_{\text{Cr}_2\text{O}_3(\text{s})} \quad (1C)$$

$$\log K_{(2)} = 2 \log K_{\text{CrO}(\text{g})} + \frac{1}{2} \log K_{\text{O}_2(\text{g})} - \log K_{\text{Cr}_2\text{O}_3(\text{s})} \quad (2C)$$

$$\log K_{(3)} = 2 \log K_{\text{CrO}_2(\text{g})} - \frac{1}{2} \log K_{\text{O}_2(\text{g})} - \log K_{\text{Cr}_2\text{O}_3(\text{s})} \quad (3C)$$

$$\log K_{(4)} = 2 \log K_{\text{CrO}_3(\text{g})} - \frac{3}{2} \log K_{\text{O}_2(\text{g})} - \log K_{\text{Cr}_2\text{O}_3(\text{s})} \quad (4C)$$

$$\begin{aligned} \log K_{(5)} = & 2 \log K_{\text{CrO}_2(\text{OH})(\text{g})} - \log K_{\text{O}_2(\text{g})} - \log K_{\text{H}_2\text{O}(\text{g})} \\ & - \log K_{\text{Cr}_2\text{O}_3(\text{s})} \end{aligned} \quad (5\text{C})$$

By definition  $\log K_{\text{O}_2(\text{g})}$  is zero at all temperatures. By combining equations (1B) to (5B) with (1C) to (5C) respectively, the pressures of the various gaseous species are obtained in terms of the log K's and pressures of  $\text{O}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$ :

$$\log P_{\text{Cr}(\text{g})} = \log K_{\text{Cr}(\text{g})} - \frac{1}{2} \log K_{\text{Cr}_2\text{O}_3(\text{s})} - \frac{3}{4} \log P_{\text{O}_2(\text{g})} \quad (1\text{D})$$

$$\log P_{\text{CrO}(\text{g})} = \log K_{\text{CrO}(\text{g})} - \frac{1}{2} \log K_{\text{Cr}_2\text{O}_3(\text{s})} - \frac{1}{4} \log P_{\text{O}_2(\text{g})} \quad (2\text{D})$$

$$\log P_{\text{CrO}_2(\text{g})} = \log K_{\text{CrO}_2(\text{g})} - \frac{1}{2} \log K_{\text{Cr}_2\text{O}_3(\text{s})} + \frac{1}{4} \log P_{\text{O}_2(\text{g})} \quad (3\text{D})$$

$$\log P_{\text{CrO}_3(\text{g})} = \log K_{\text{CrO}_3(\text{g})} - \frac{1}{2} \log K_{\text{Cr}_2\text{O}_3(\text{s})} + \frac{3}{4} \log P_{\text{O}_2(\text{g})} \quad (4\text{D})$$

$$\begin{aligned} \log P_{\text{CrO}_2(\text{OH})(\text{g})} = & \log K_{\text{CrO}_2(\text{OH})(\text{g})} - \frac{1}{2} \log K_{\text{H}_2\text{O}(\text{g})} + \frac{1}{2} \log P_{\text{O}_2(\text{g})} \\ & - \frac{1}{2} \log K_{\text{Cr}_2\text{O}_3(\text{s})} + \frac{1}{2} \log P_{\text{H}_2\text{O}(\text{g})} \end{aligned} \quad (5\text{D})$$

#### Thermodynamic Data

The  $K_p$  values for the gaseous species in the Cr-O-H system and for  $\text{Cr}_2\text{O}_3(\text{s})$  were taken from the literature. The thermodynamic information necessary to construct the tables of  $\log K_p$  as a function of temperature is derived for the Cr-O molecules from vaporization studies on solid chromium oxides. The Knudsen cell mass spectrometric study of Grimley et al. (ref. 4) of the vaporization of  $\text{Cr}_2\text{O}_3(\text{s})$ , along with an estimation of the molecular structure parameters for the  $\text{CrO}(\text{g})$ ,  $\text{CrO}_2(\text{g})$  and  $\text{CrO}_3(\text{g})$  molecules by Schick et al. (ref. 6), provides the thermochemical quantities necessary for the construction of thermodynamic

tables. A recent investigation by Kim and Belton (ref. 7) who used the transpiration technique resulted in apparently more reliable thermodynamic information for  $\text{CrO}_3(\text{g})$ . These data were preferred in the present calculations. The thermodynamic data for  $\text{Cr}(\text{g})$  were taken from Schick (ref. 6) while those for  $\text{Cr}_2\text{O}_3(\text{s})$  were taken from Wicks and Block (ref. 8). The results of Kim and Belton (ref. 7) were used for  $\text{CrO}_2(\text{OH})(\text{g})$ .

Equations (4D) and (5D) can be put into a more convenient form by substituting the expressions for the free energy of formation of  $\text{CrO}_3(\text{g})$  and  $\text{CrO}_2(\text{OH})(\text{g})$  given by Kim and Belton (ref. 7) to yield:

$$\log P_{\text{CrO}_3(\text{g})} = -1.299 \times 10^4 / T + 3.082 + \frac{3}{4} \log P_{\text{O}_2(\text{g})} \quad (4\text{E})$$

$$\log P_{\text{CrO}_2(\text{OH})(\text{g})} = 1.123 \times 10^4 / T + 3.147 + \frac{1}{2} \log P_{\text{O}_2(\text{g})} + \frac{1}{2} \log P_{\text{H}_2\text{O}(\text{g})} \quad (5\text{E})$$

#### Thermochemical Diagrams

The results of the calculations of vapor pressure of the Cr-O molecules are presented in figures 1 to 13 for 100° temperature intervals from 900 to 1800° K (temperature above 1600° K are only of academic interest) and at 1073°, 1273° and 1473° K (800°, 1000° and 1200° C). The plots of  $\log P_{\text{Cr}(\text{g})}$ ,  $\log P_{\text{CrO}(\text{g})}$ ,  $\log P_{\text{CrO}_2(\text{g})}$ , and  $\log P_{\text{CrO}_3(\text{g})}$  as a function of  $\log P_{\text{O}_2(\text{g})}$  and temperature were calculated by the use of equations (1D), (2D), (3D), and (4D), respectively. Equation (4E) was used to construct the preferred plots for  $\log P_{\text{CrO}_3(\text{g})}$  based on the data of Kim and Belton (ref. 7).

The partial pressures may be easily calculated at any other temperature of interest by the proper interpolation of  $\log K_p$  values given in Schick (ref. 6) for  $\text{Cr}(\text{g})$ ,  $\text{CrO}(\text{g})$ ,  $\text{CrO}_2(\text{g})$  and the use of equations (1D), (2D), (3D), and equation (4E) for  $\text{CrO}_3(\text{g})$ .

Equation (5E) was used to construct the plots for  $\log P_{\text{CrO}_2(\text{OH})(\text{g})}$ . The pressures of  $\text{CrO}_2(\text{OH})$  as a function of  $P_{\text{O}_2(\text{g})}$  and  $P_{\text{H}_2\text{O}(\text{g})}$  are presented in figures 14 and 15 for 1273° K (1000° C) and 1473° K (1200° C). The pressures at any additional temperatures can be calculated by the use of equation (5E).



### III. MASS SPECTROMETRIC IDENTIFICATION OF VAPORIZING SPECIES

#### Purpose

The purpose of the mass spectrometer experiments was to identify the species vaporizing from the surface of oxidized TD-NiCr and to obtain experimental evidence to support the thermodynamic calculations of the vapor composition. The species of major interest were  $\text{CrO}_3(\text{g})$  and  $\text{CrO}_2(\text{g})$ . The calculations indicated that  $\text{CrO}_3(\text{g})$  and  $\text{CrO}_2(\text{g})$  would be difficult to observe and that high temperatures near the melting point of TD-NiCr would be required to achieve adequate vapor pressures of these species. In any case the calculations indicated that the observations would be made near the minimum limit of detectability of the apparatus. Furthermore, the calculations indicated that the other species ( $\text{CrO}(\text{g})$  and  $\text{Cr}(\text{g})$ ) were too low in intensity to observe by the normal techniques.

#### Experimental Apparatus

Strips of TD-NiCr ( $1/16'' \times 0.040'' \times 1-1.5''$ ) were mounted on tantalum posts in the source of a modified CEC 21-110 double-focusing mass spectrometer. The mass spectrometer and associated equipment have been described in detail previously (refs. 9 and 10). The high resolution and sensitivity of the mass spectrometer permit the observation of molecular species of low partial pressure ( $10^{-3}$  -  $10^{-10}$  atm) effusing from a Knudsen cell or vaporizing from the surface of a filament. The geometry of the mounting assembly was such that the strip was parallel to and facing the ion source entrance slit (see fig. 2 of ref. 9). The distance between the strip and the ionizing region of the mass spectrometer was the minimum possible, that is approximately  $1.5''$ . The TD-NiCr strips were heated resistively by a low voltage DC power supply.

#### Experiments with Unoxidized TD-NiCr

Several separate TD-NiCr strips were used in various experiments. Each strip was used until it failed due to melting and/or oxidation. When an unoxidized strip of TD-NiCr was heated to above  $1250^\circ \text{K}$ , the  $\text{Cr}^+$  and  $\text{Ni}^+$  ions resulting from the ionization of  $\text{Cr}(\text{g})$  and  $\text{Ni}(\text{g})$  which were vaporizing from the strip were easily observed. The background pressure in the sample vacuum chamber of the mass spectrometer was generally in the low  $10^{-8}$  to high  $10^{-8}$  torr range as recorded by a Bayard-Alpert type ionization gauge attached to the chamber. The oxygen partial pressure ( $\text{P}_{\text{O}_2}(\text{g})$ ) under these conditions was probably less than  $1/10$  of the total

measured pressure. The observation of  $\text{Cr}^+$  and  $\text{Ni}^+$  established that the sensitivity and resolution of the mass spectrometer were adequate and provided markers for mass measurement, ion focusing, and sample position alignment.

The surface temperature at the center of the TD-NiCr strip was read by the use of a calibrated Micro Optical pyrometer. An emissivity of 0.40 was used for the unoxidized TD-NiCr (ref. 11). The measured temperatures were corrected for the absorption of the viewing window. The window was protected by a magnetically actuated shutter assembly.

#### Experiments with Oxidized TD-NiCr

To oxidize a strip of TD-NiCr, oxygen gas was admitted to the system at a controlled rate by a leak valve. The oxygen pressure in the system was assumed to be equal to the sample chamber total pressures as read by the ionization gauge. Because the system was continuously being pumped, a constant flow of oxygen was required to maintain any given pressure. The range of attainable pressures was from  $1 \cdot 10^{-6}$  to  $5 \cdot 10^{-4}$  torr. The operating requirements of the mass spectrometer ion source precluded operation at higher pressures. No absolute pressure calibration of the ion gauge was made.

One striking observation was that the intensity of  $\text{Cr}^+$  fell off drastically and instantaneously when oxygen was admitted to the system. In general, the TD-NiCr strips were oxidized for from 0.5 to 1.5 hours at 1150 to 1165° C with a  $P_{\text{O}_2}(\text{g})$  of  $3\text{-}5 \cdot 10^{-4}$  torr. This treatment results in a layer of  $\text{Cr}_2\text{O}_3(\text{s})$  on the surface of the sample. Following this treatment a search was made for the vaporizing species. Ions containing chromium and oxygen were observed in two experiments.

In the first experiment,  $\text{CrO}_3^+$  was identified at a strip temperature of 1660° K and an oxygen pressure of about  $5 \cdot 10^{-4}$  torr. The temperature of the oxidized TD-NiCr strip was obtained using an emissivity of 0.82 (ref. 12). The recorded intensity for this species indicated that its partial pressure was in the  $10^{-8}$  to  $10^{-10}$  torr range and in the general area predicted by the calculations for the  $P_{\text{CrO}_3}(\text{g})$  at 1600° to 1700° K.

Before a thorough search for the other species was completed, strip failure ended the experiment.

We believe that the temperatures recorded for the TD-NiCr samples were correct to  $\pm 15$  degrees. The reported melting point for Ni-20% Cr is about 1400° C (ref. 13). The melting or softening point for TD-NiCr is expected to be the same as this  $\pm 20$  degrees. The samples used in our experiments always failed when the temperature approached  $1440 \pm 20^\circ \text{C}$ .

For the second experiment, the TD-NiCr strip was oxidized at a  $P_{O_2}(g)$  of about  $4.7 \cdot 10^{-4}$  torr for 50 minutes at 1150 to 1165° C. The temperature was raised to 1693° K and peaks corresponding to  $CrO_2^+$  and  $CrO_3^+$  were observed. The measured ratio  $I_{CrO_2^+}/I_{CrO_3^+} \approx P_{CrO_2(g)}/P_{CrO_3(g)}$  was approximately 5. Considering the temperature and pressure uncertainties this is taken to be a good verification of the calculations. Furthermore this result indicates that the values of Kim and Belton (ref. 7) are to be preferred. The temperature of the strip was then raised about 15° in order to obtain higher ion intensities for more reliable intensity measurements but the strip failed before further measurements could be made.

#### IV. DISCUSSION

##### Equilibrium Vaporization under Oxidizing Conditions

The equilibrium vapor compositions for the Cr-O system presented graphically in figures 1 to 13 show that  $CrO_3(g)$  and  $CrO_2(g)$  are the species which account for the greatest fraction of chromium vaporization under the most relevant conditions of temperature and oxygen pressure. As stated previously, the calculations for  $CrO_3(g)$  have been carried out using the thermodynamic data from both Grimley et al. (ref. 4) and Kim and Belton (ref. 7) and we believe that the data of Kim and Belton are more reliable. It is apparent from the plots of  $\log P_{CrO_3(g)}$  versus  $\log P_{O_2(g)}$

that the data of Kim and Belton labeled as  $CrO_3$  (Belton) lead to values of  $P_{CrO_3(g)}$  at least an order of magnitude higher than the results of

Grimely et al. for all temperatures considered. The  $CrO(g)$  and  $Cr(g)$  species become important only at the highest temperatures and low oxygen pressures. The calculations show that, for the relatively high oxygen pressures expected to be encountered for space shuttle and turbine engine applications,  $CrO_3(g)$  is the only species to be considered for any practical purposes. Therefore, in figure 16, we give the pressure of  $CrO_3(g)$  as a function of temperature and oxygen pressure. Starting with the vapor pressures presented in figure 16 the maximum possible, or equilibrium, rate of vaporization of the species  $CrO_3(g)$  can be calculated by the equation:

$$G_{CrO_3} \text{ (gm/cm}^2\text{/sec)} = \frac{P_{CrO_3} \text{ (atm)}}{2.255 \times 10^{-2}} \left( \frac{M_{CrO_3}}{T} \right)^{1/2} \quad (6)$$

where  $M_{CrO_3}$  is the molecular weight of  $CrO_3$ . This is the specific form of the general Hertz-Langmuir equation which gives the rate of weight loss per unit area,  $G_i$ , for any species  $i$ :

$$G_i \text{ (gm/cm}^2\text{/sec)} = \frac{P_i \text{ (atm)} \left( \frac{M_i \text{ gm}}{\text{mole}} \right)^{1/2}}{2.255 \times 10^{-2} T \text{ (}^\circ\text{K)}} \quad (7)$$

The rate of evaporation of Cr metal due to the vaporization of the molecular species  $i$  which contain Cr can be obtained by multiplying equation (7) by the ratio  $(M_{\text{Cr}}/M_i)^{1/2}$  to give

$$G_{\text{Cr}} \text{ (gm/cm}^2\text{/sec)} = \frac{P_i \text{ (atm)} \left( \frac{M_{\text{Cr}}}{T} \right)^{1/2}}{2.255 \times 10^{-2}} \quad (8)$$

In figure 17 the rate of evaporation of Cr calculated by the use of equation (8) is shown as a function of temperature and oxygen pressure. At oxygen pressures above  $10^{-3}$  atm.  $\text{CrO}_3(\text{g})$  is the only significant vaporization product. However, at lower oxygen pressures and high temperatures  $\text{CrO}_2(\text{g})$  also becomes a significant product. Hence, to get the total  $G_{\text{Cr}}$  the contributions from both  $\text{CrO}_3$  and  $\text{CrO}_2$  must be added and this was done for the curves shown in figure 17. Where the  $\text{CrO}_2(\text{g})$  species becomes significant is manifested by an upward curvature to the lines shown in figure 17.

The rate of recession of Cr from the TD-NiCr surface can easily be computed for the equilibrium situation by multiplying the values of the Cr vaporization rate by  $0.12 \text{ cm}^3/\text{gm}$  which is our estimate of the specific volume of Cr in the alloy. Therefore the rate of recession,  $R_{\text{Cr}}$ , of metal from oxidized TD-NiCr can be calculated by the following equations:

$$R_{\text{Cr}} \text{ (cm/sec)} = \frac{P_i \text{ (atm)}}{T^{1/2}} (3.8 \times 10^1) \quad (9)$$

or

$$R_{\text{Cr}} \text{ (mils/hr)} = \frac{P_i \text{ (atm)}}{T^{1/2}} (5.4 \times 10^7) \quad (10)$$

## Equilibrium Vaporization in the Presence of $\text{H}_2\text{O}(\text{g})$

The calculations of the pressures of  $\text{CrO}_2(\text{OH})(\text{g})$  demonstrate that this species will be quite important in the vaporization of TD-NiCr in atmospheres containing both  $\text{O}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$ . For example, at  $1273^\circ\text{K}$  with  $P_{\text{O}_2}(\text{g})$  and  $P_{\text{H}_2}(\text{g})$  both equal to  $10^{-2}$  atm. the equilibrium pressure of  $\text{CrO}_2(\text{OH})(\text{g})$  is greater than that of  $\text{CrO}_3(\text{g})$  by a factor of 2.2.

### Experimental Confirmation

$\text{CrO}_2(\text{g})$  and  $\text{CrO}_3(\text{g})$  were positively identified in the mass spectrometric experiments at  $1693^\circ\text{K}$ . The measured ratio of these species indicates that the pressures of the species are of the same order of magnitude as calculated using the preferred data for  $\text{CrO}_3(\text{g})$ . This result is taken as an experimental verification of the calculations.

Because the data for this experimental confirmation is limited, additional experiments of a more complicated nature were considered for obtaining more data, particularly for observing the vaporizing species at higher oxygen pressures, closer to those expected for the space shuttle applications. In order to achieve higher oxygen pressures and simultaneously mass spectrometrically sample the vapor, a sophisticated multiple differentially pumped apparatus seems to be required. However, it was felt that because of geometrical and spatial considerations a diminishing return would result. The increased sample to ion source distance and other factors such as the mean free path of the molecules would lower the detection limit of the setup, and thus reduce the gains made by using higher oxygen pressures. Therefore we conclude that methods other than mass spectrometry would probably be more fruitful for further studies.

## V. CONCLUDING REMARKS

### Actual Behavior of Oxidized TD-NiCr

The calculations of the vaporization rates of  $\text{CrO}_3(\text{g})$  show that the vaporization of oxidized TD-NiCr may pose a serious problem with respect to the high temperature structural capabilities of this material. It must be emphasized that the calculations describe the equilibrium situation for the oxidative vaporization of  $\text{Cr}_2\text{O}_3(\text{s})$ . Kinetic effects, diffusion, modifications or anomalies in surface composition and characteristics, and other factors may influence the vaporization in significant ways. It is felt that the equilibrium vaporization rate may be a reasonable approxi-

mation to the situation which will exist at high mach velocities when the vapor phase will be continuously swept away from the surface of the solid.

The  $\text{ThO}_2$  is not expected to vaporize appreciably at the temperatures of interest.<sup>2</sup> However, we expect that after significant amounts of Cr have been removed from the alloy (Cr depletion) the resulting NiO rich scale formed on the surface will vaporize to Ni(g) and NiO(g) (ref. 14). The vaporization rate is expected to be of the same order of magnitude as calculated for the chromium oxides at moderate  $\text{O}_2$  pressures ( $10^{-7}$  -  $10^{-4}$  atm.) and lower at higher  $\text{O}_2$  pressures.

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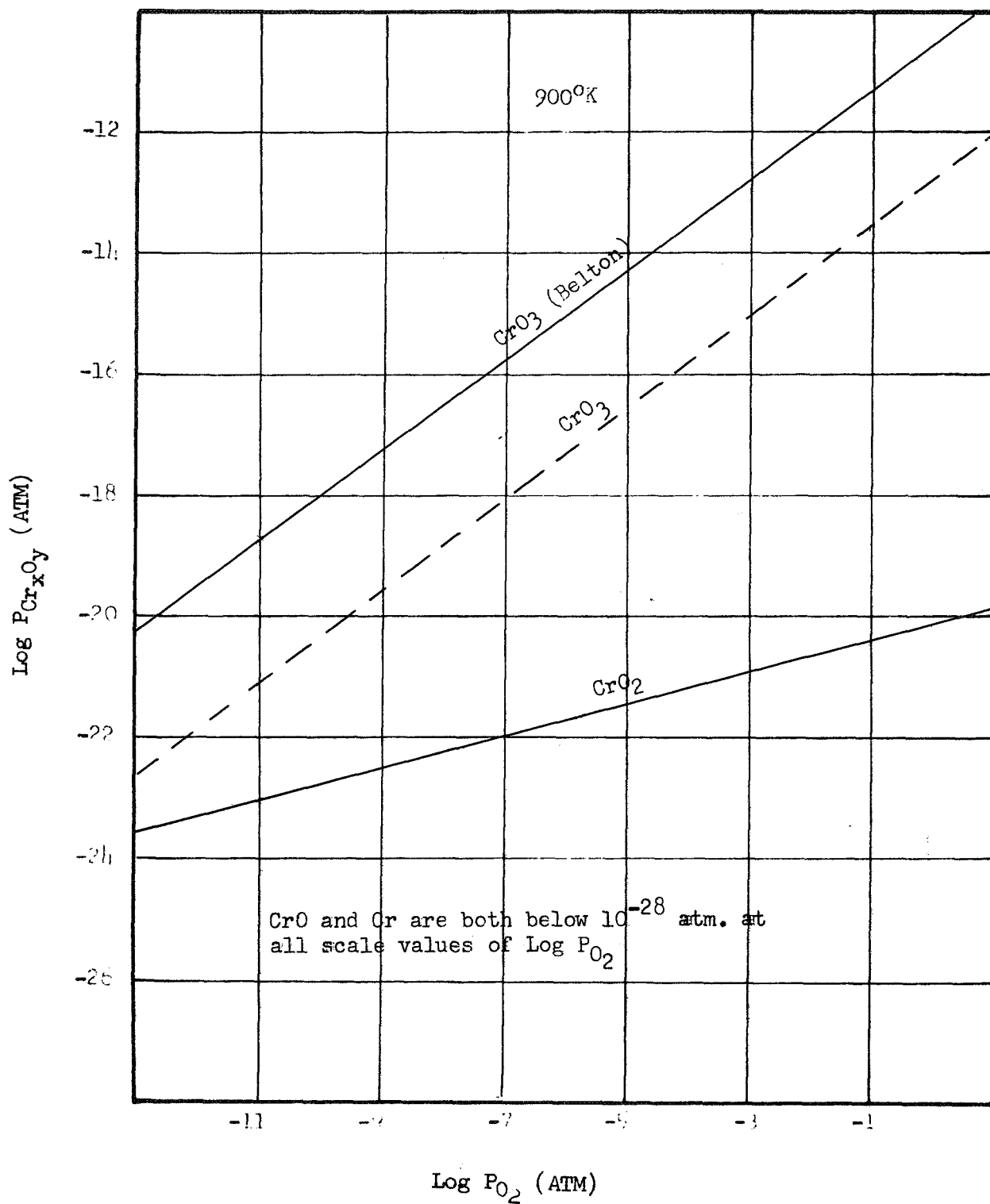


Fig. 1 Thermochemical diagram of the chromium-oxygen system at 900°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.



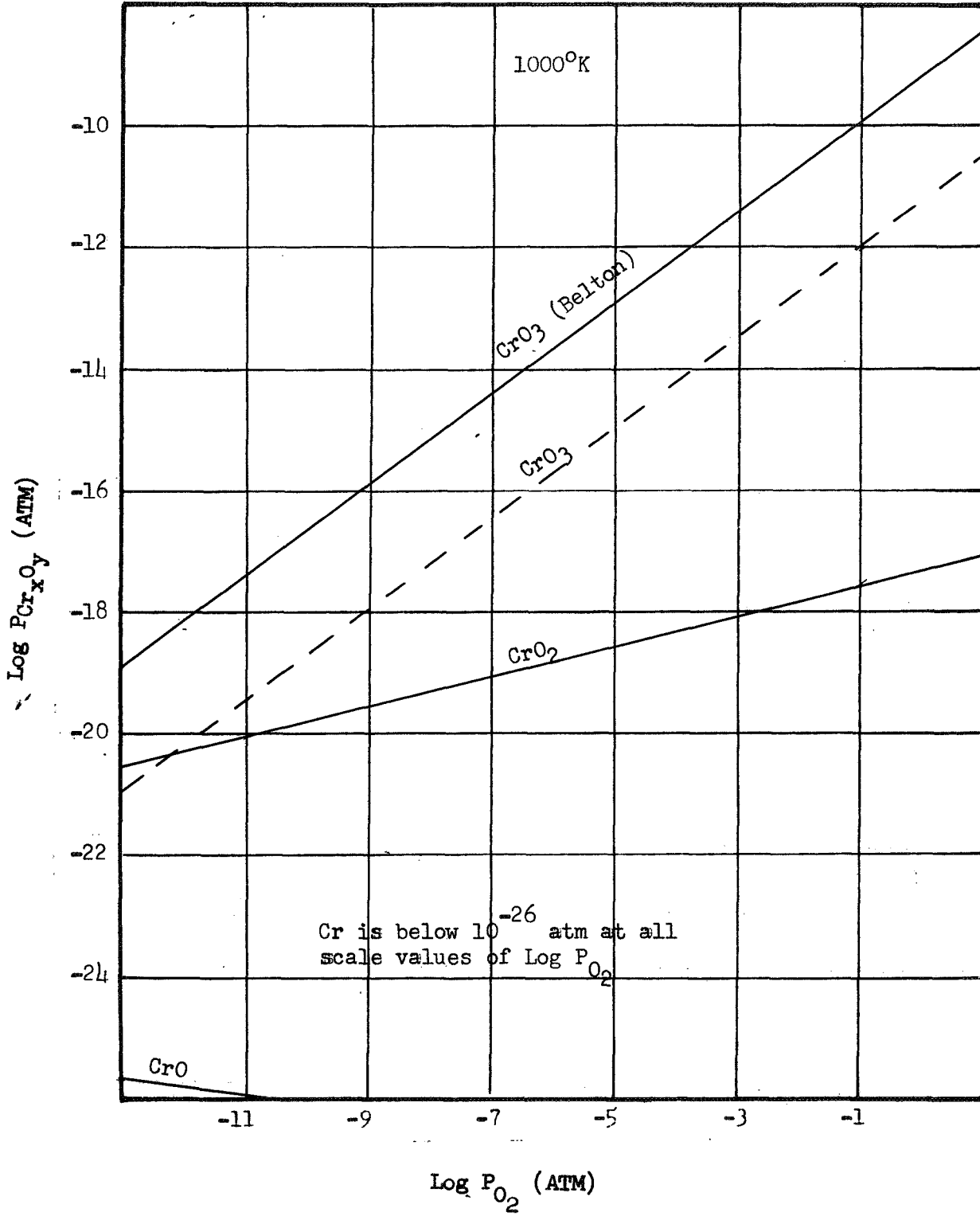


Fig. 2 Thermochemical diagram of the chromium-oxygen system at 1000°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.

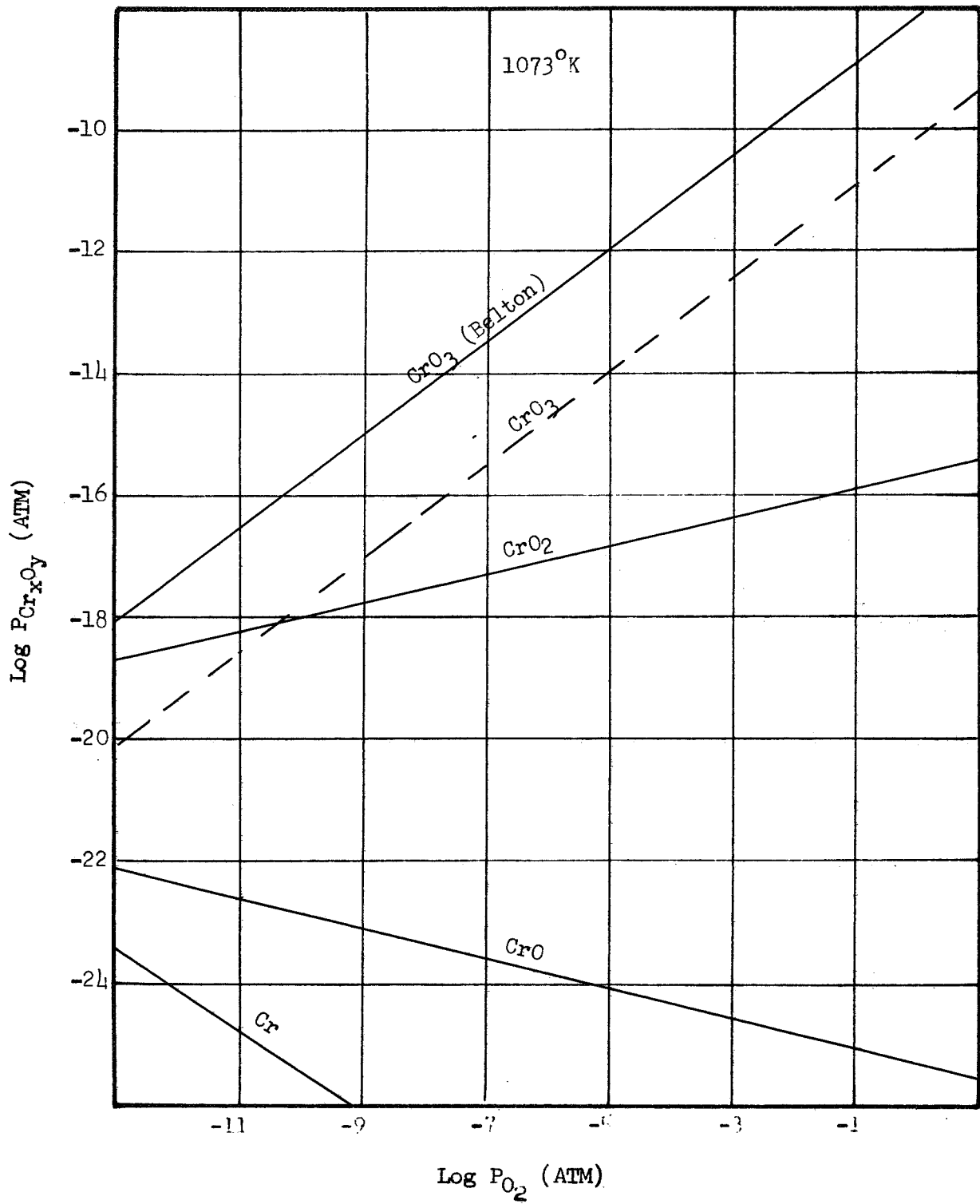


Fig. 3 Thermochemical diagram of the chromium-oxygen system at 1073°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.

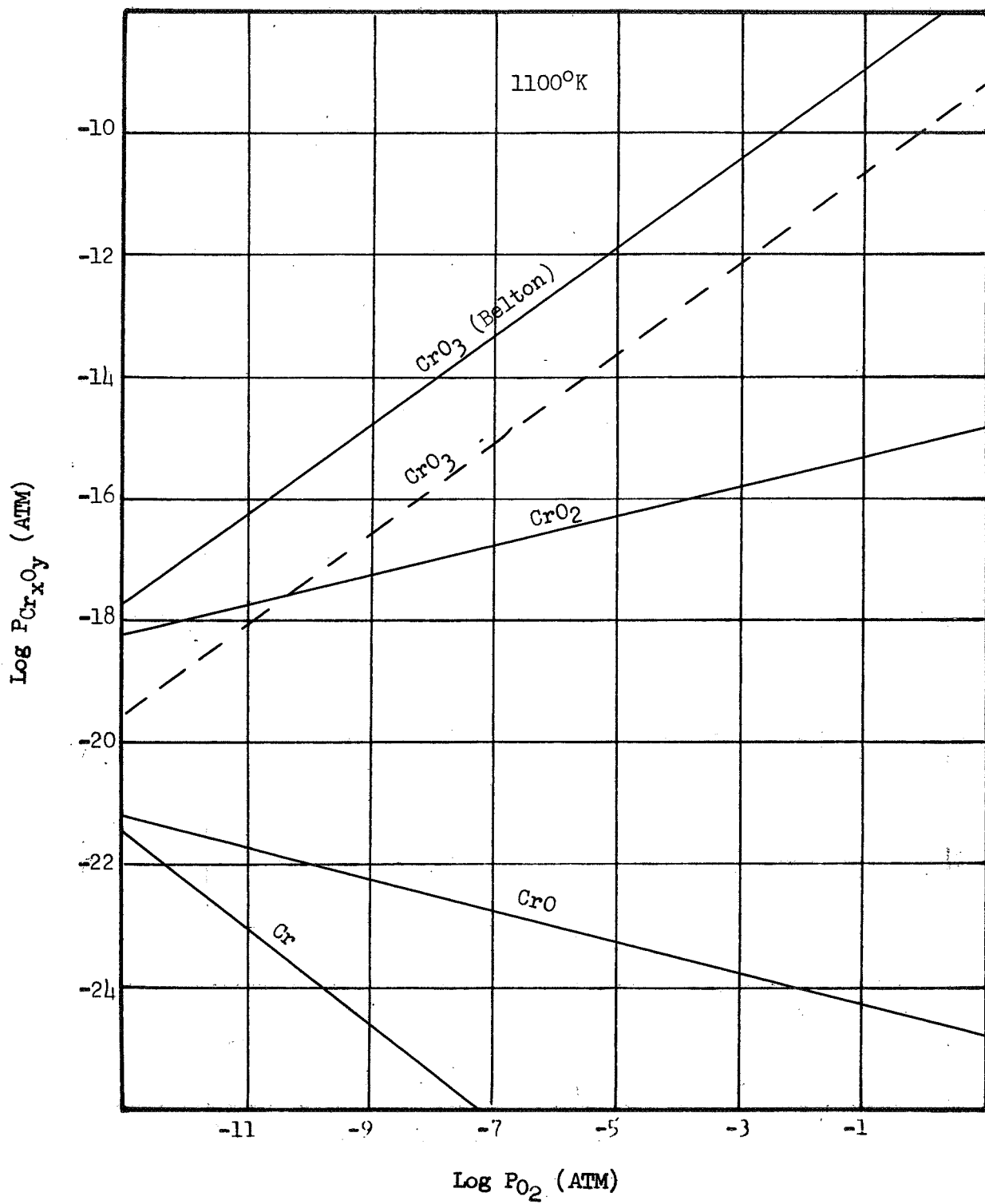


Fig. 4 Thermochemical diagram of the chromium-oxygen system at 1100°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.

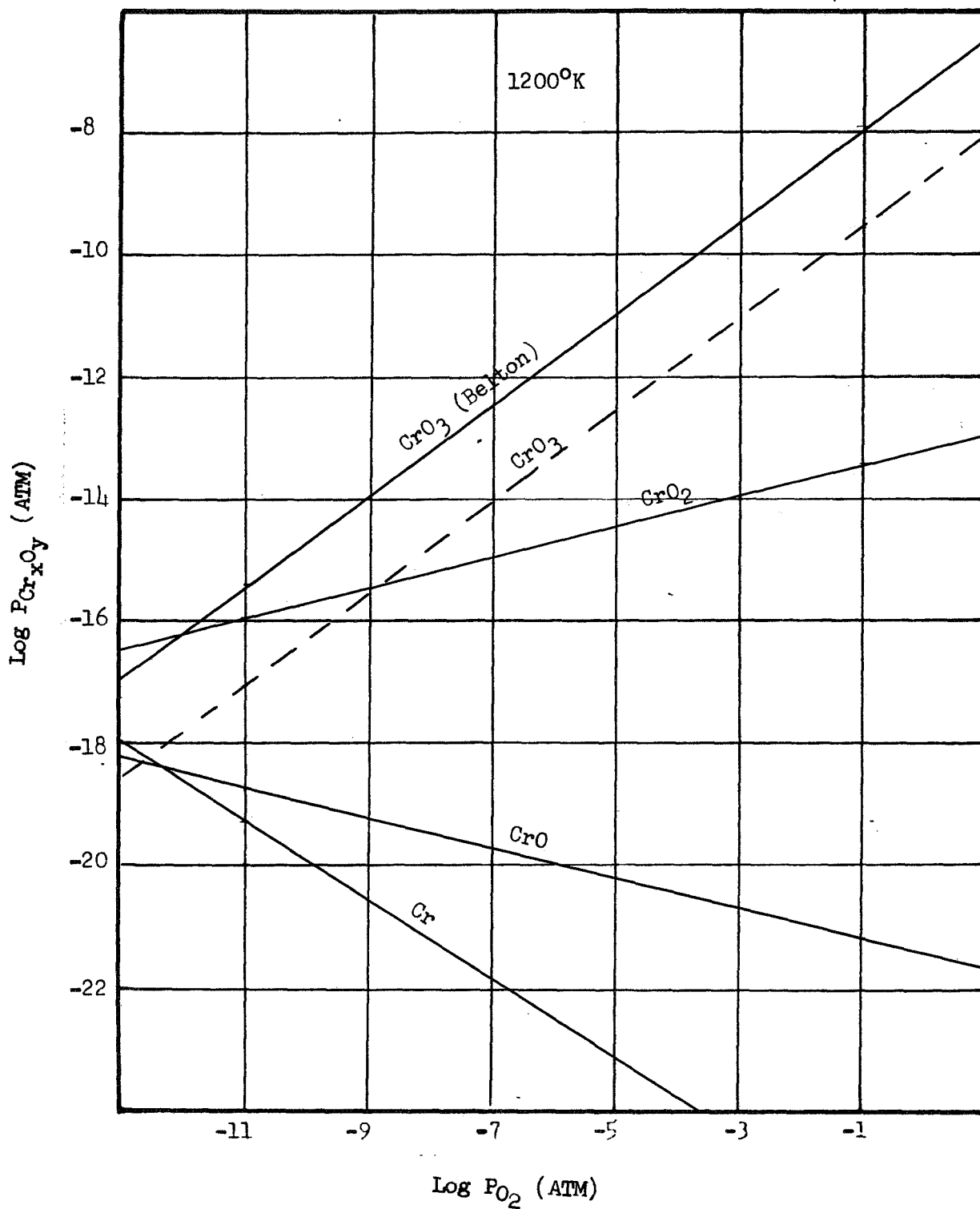


Fig. 5 Thermochemical diagram of the chromium-oxygen system at 1200°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.

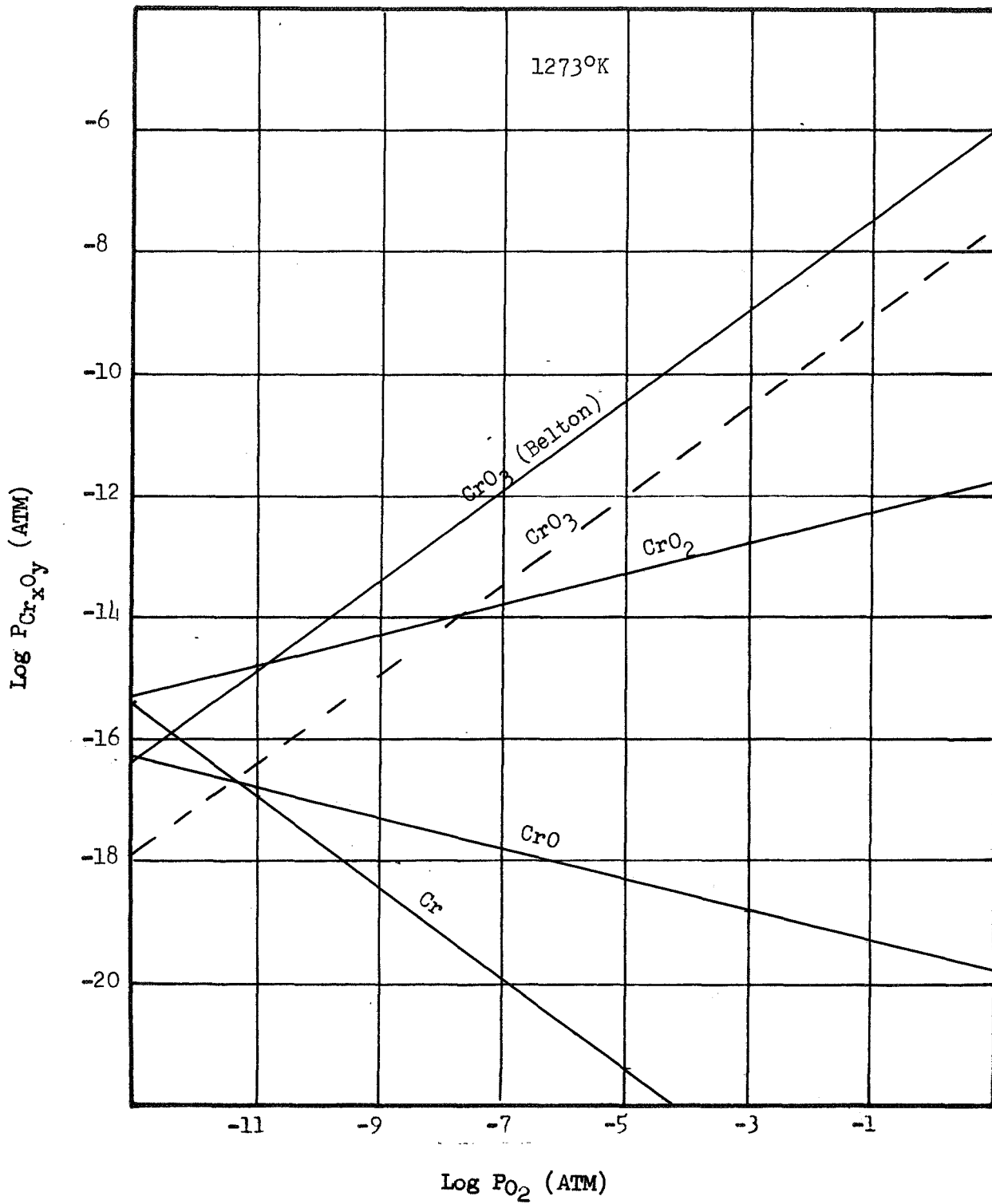


Fig. 6 Thermochemical diagram of the chromium-oxygen system at 1273°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.

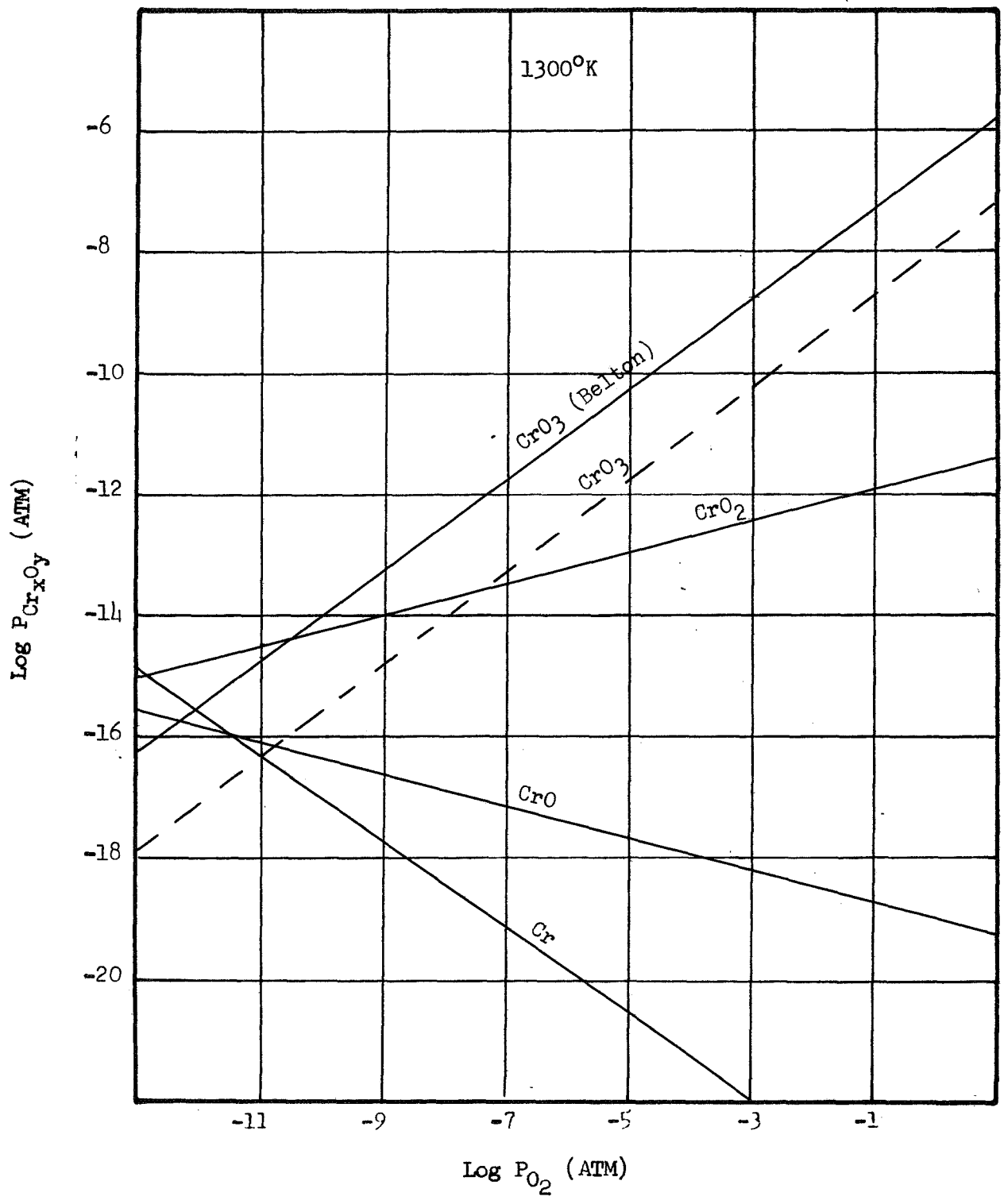


Fig. 7 Thermochemical diagram of the chromium-oxygen system at 1300°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.

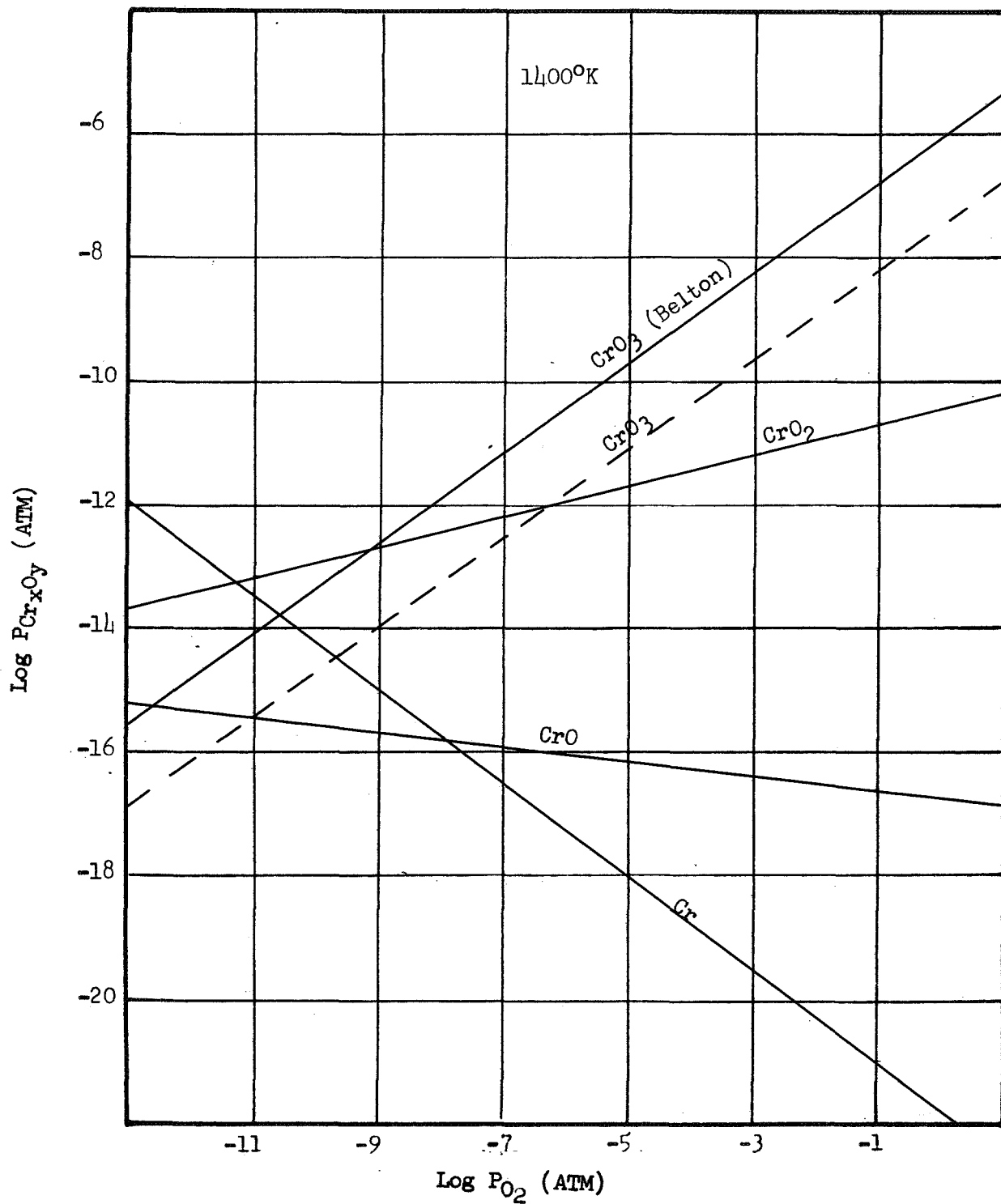


Fig. 8 Thermochemical diagram of the chromium-oxygen system at 1400°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.

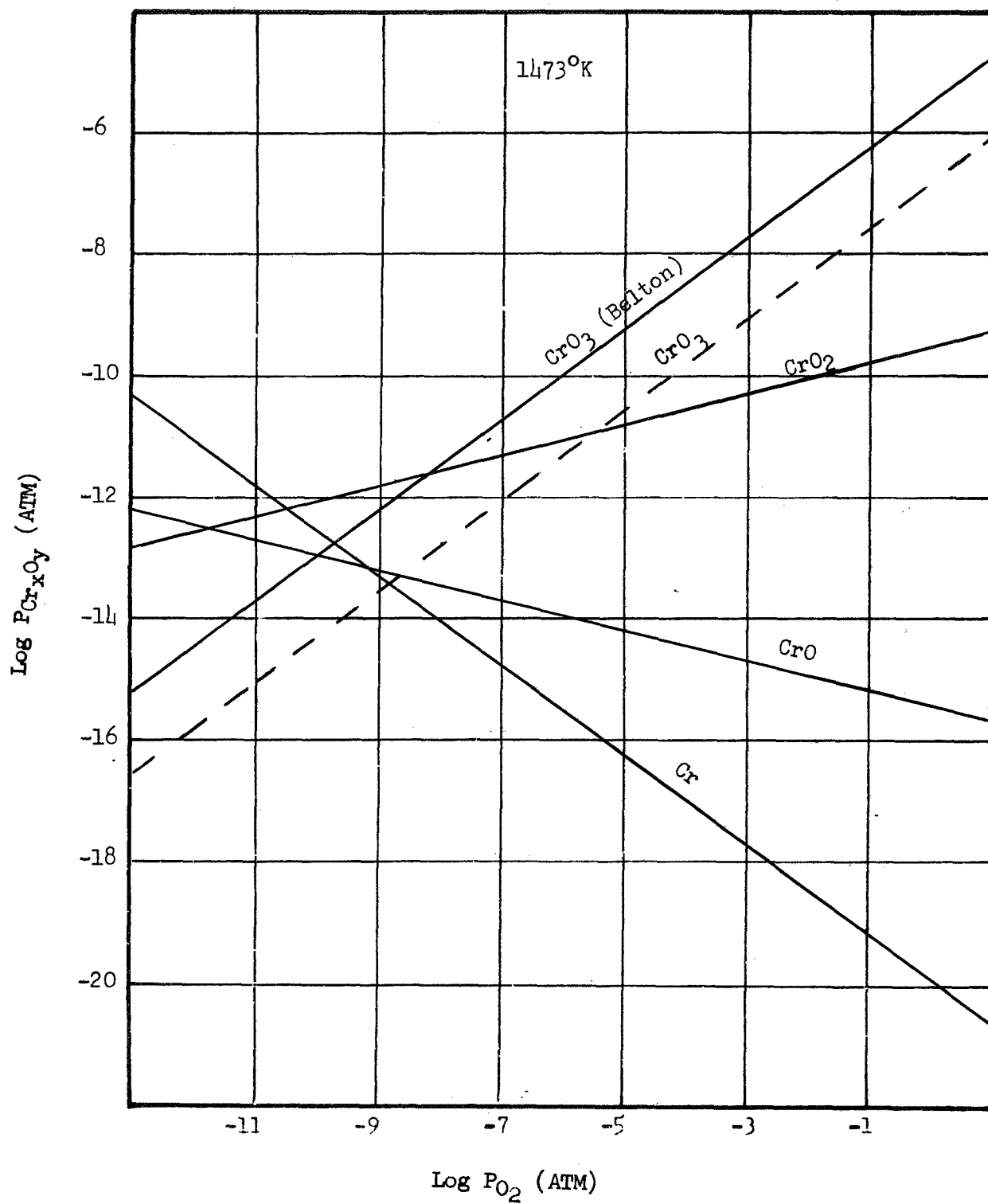


Fig. 9 Thermochemical diagram of the chromium-oxygen system at 1473°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.



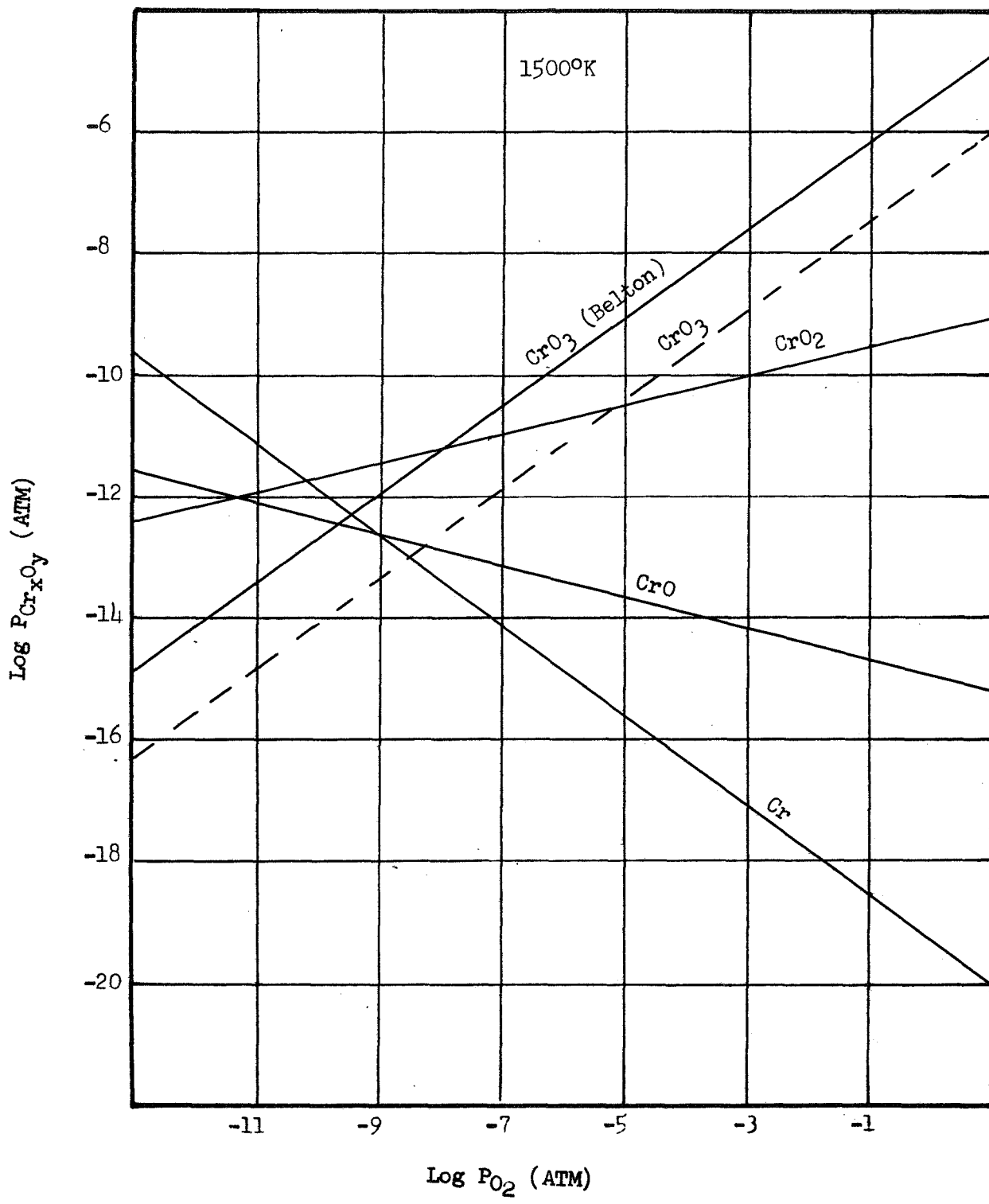


Fig. 10 Thermochemical diagram of the chromium-oxygen system at 1500°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.

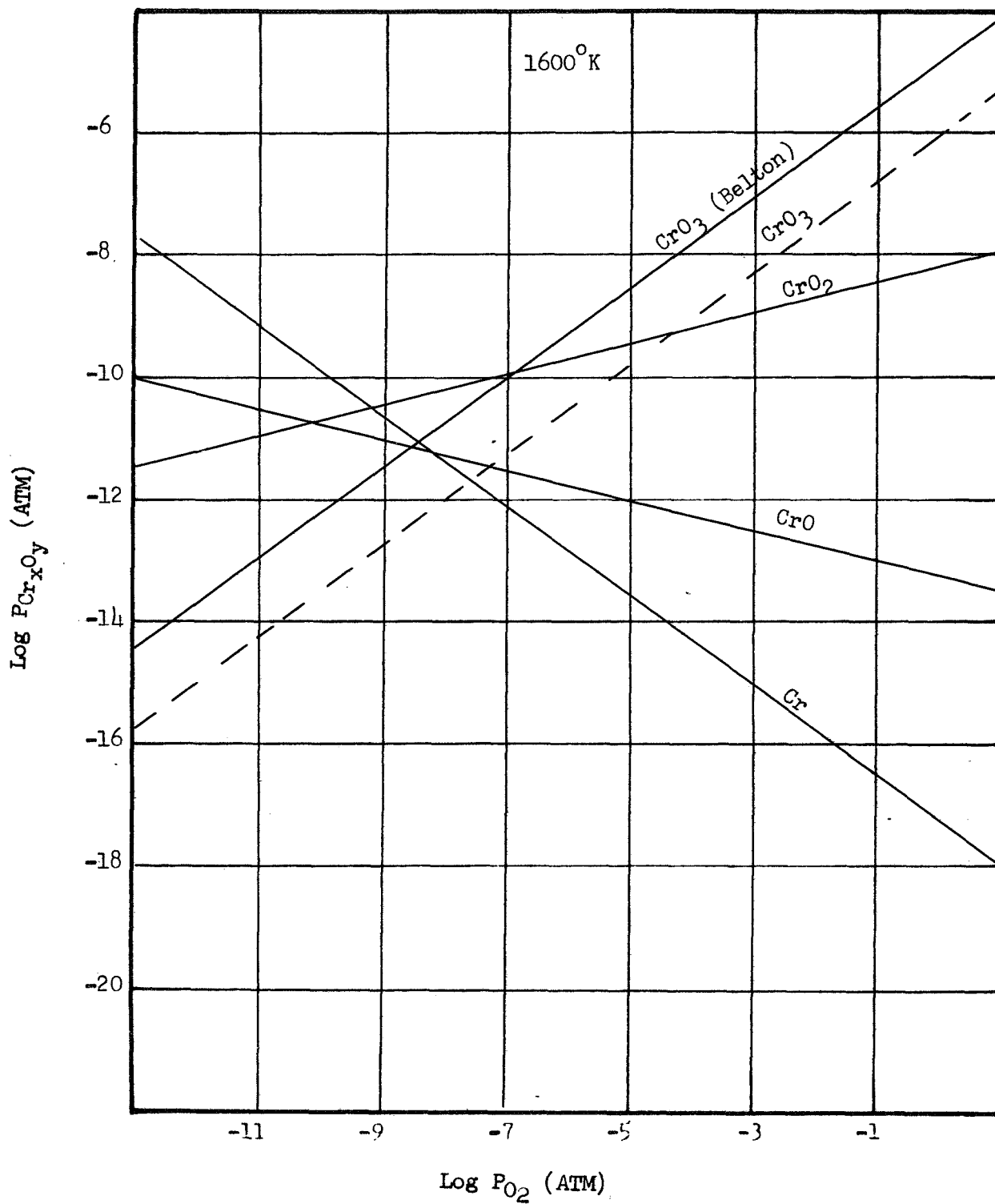


Fig. 11 Thermochemical diagram of the chromium-oxygen system at 1600°K. Stable condensed phase is Cr<sub>2</sub>O<sub>3</sub>.

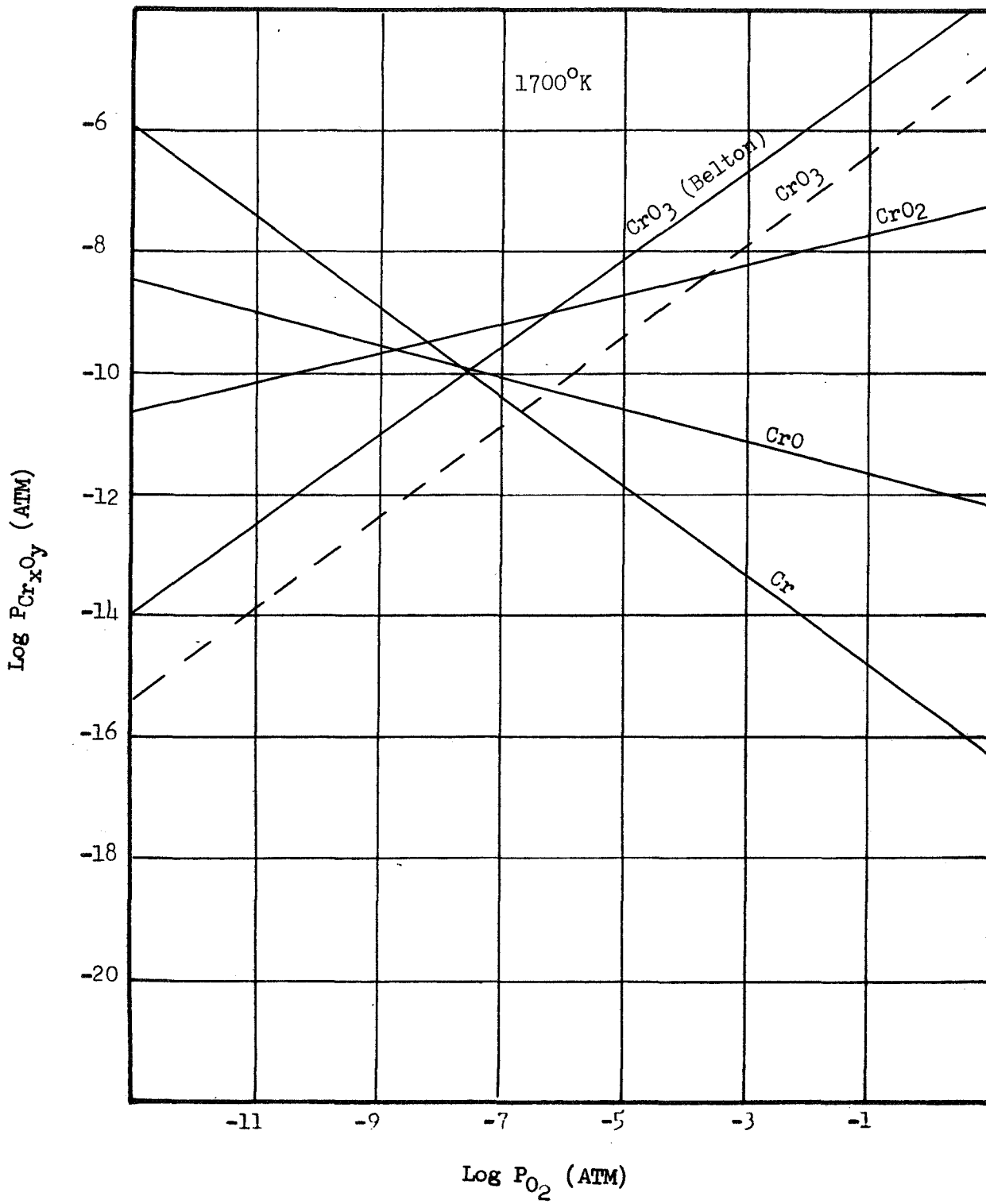


Fig. 12 Thermochemical diagram of the chromium-oxygen system at 1700°K. Stable condensed phase is  $Cr_2O_3$ .

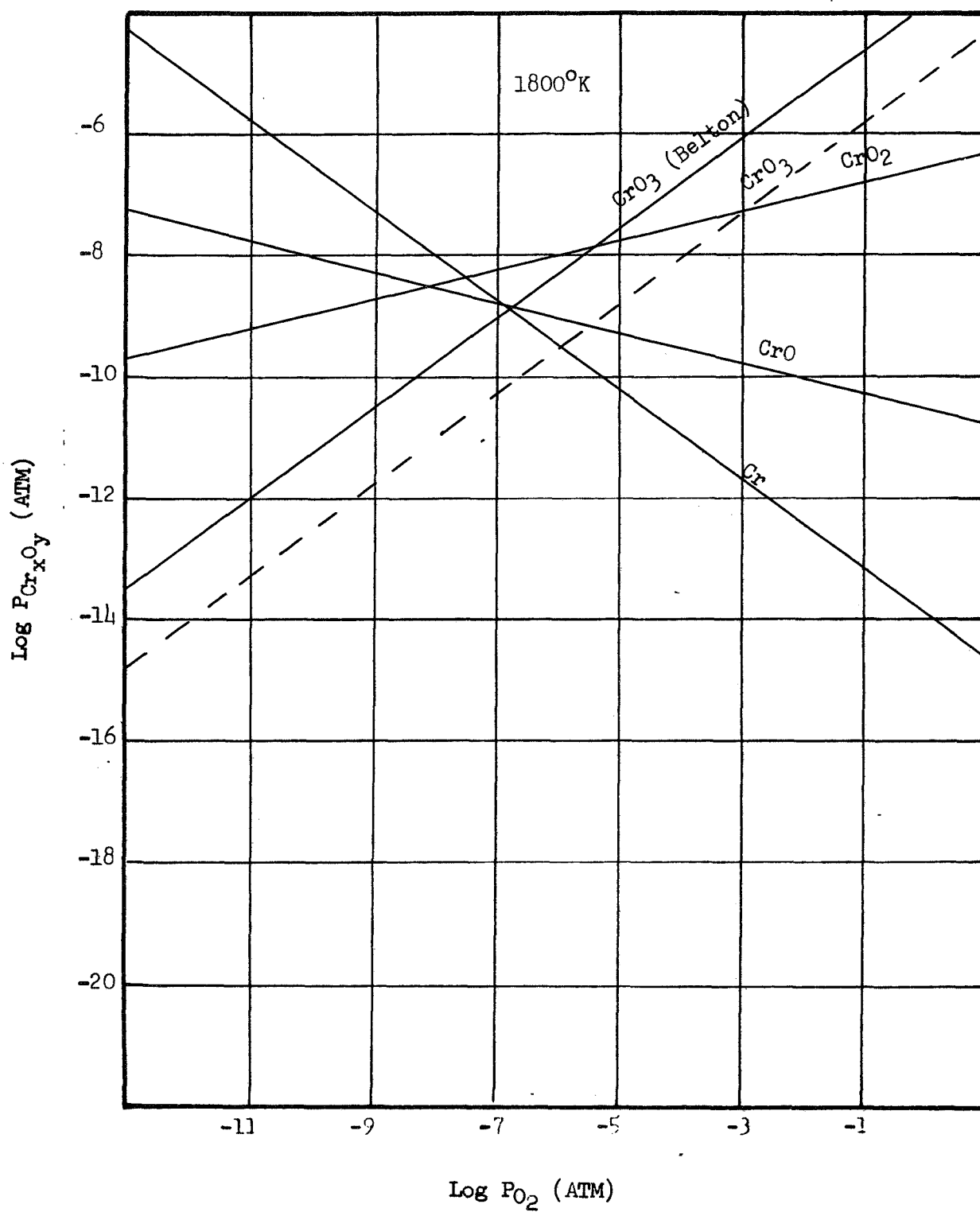


Fig. 13 Thermochemical diagram of the chromium-oxygen system at 1800°K. Stable condensed phase is  $Cr_2O_3$ .

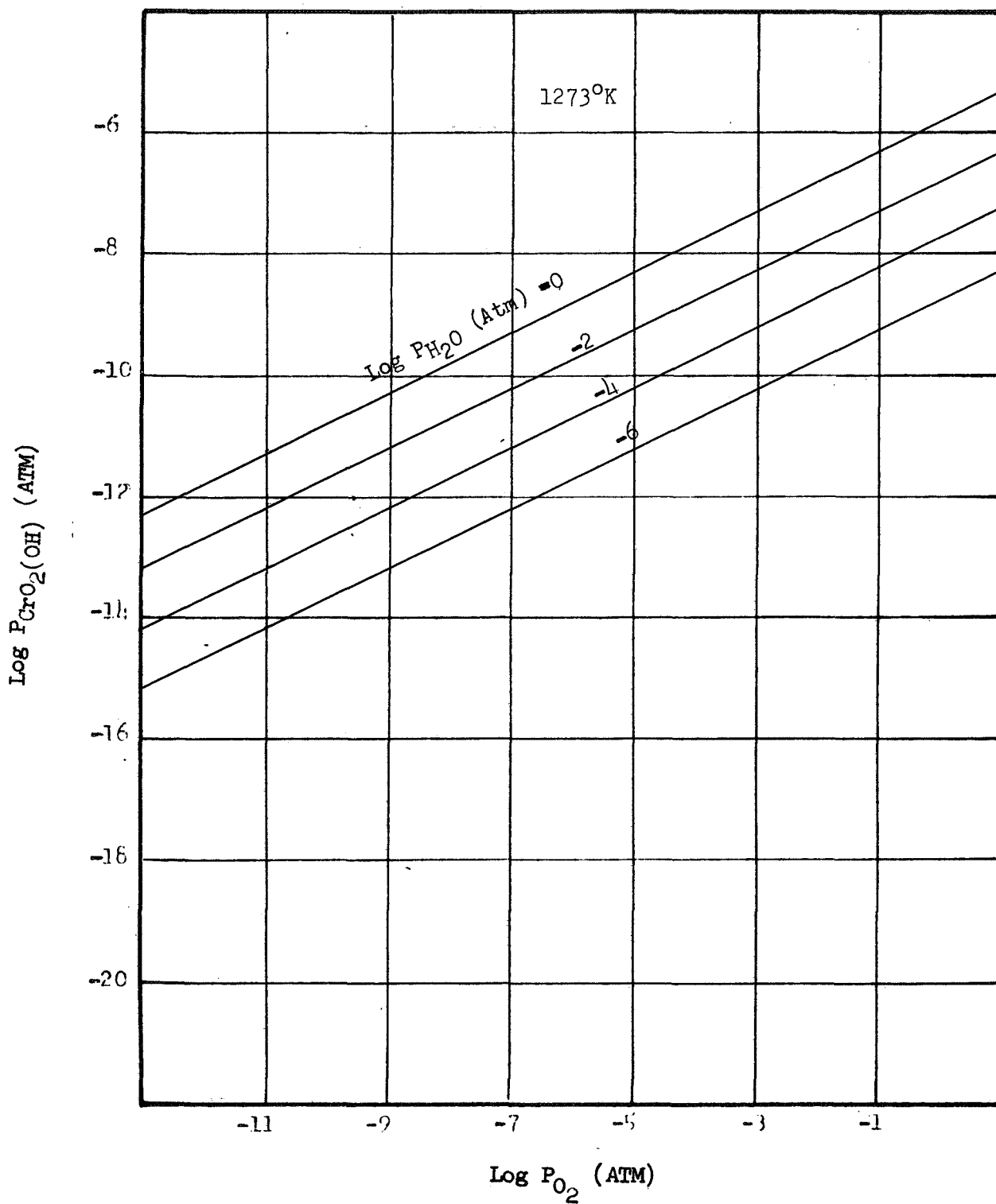


Fig. 14 Vapor pressures of  $\text{CrO}_2(\text{OH})$  (g) as a function of oxygen pressure and water vapor pressure at  $1273^\circ\text{K}$  for the system  $\text{Cr}_2\text{O}_3(\text{s})-\text{O}_2(\text{g})-\text{H}_2\text{O}(\text{g})$ .

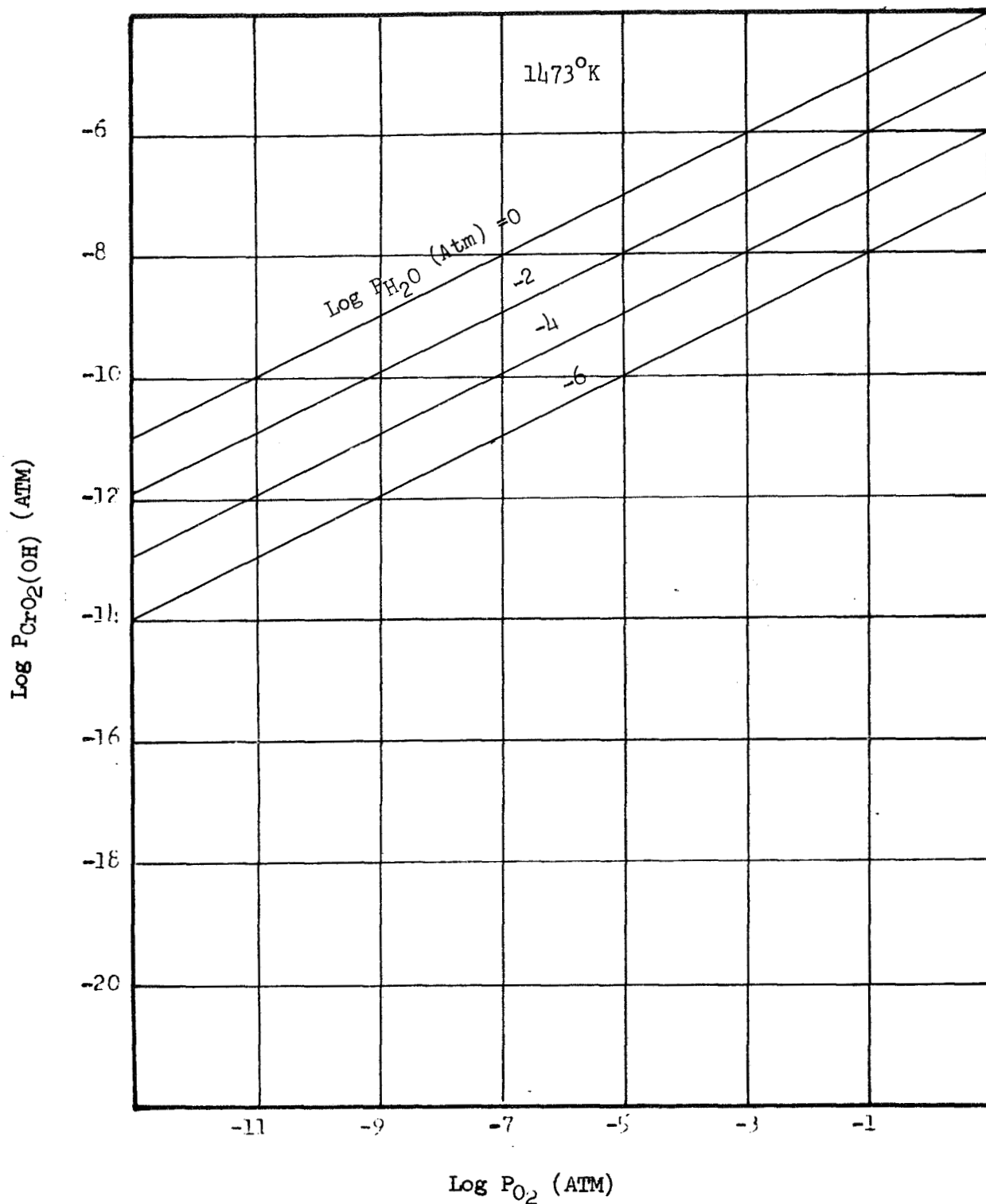


Fig. 15 Vapor pressures of  $CrO_2(OH)$  (g) as a function of oxygen pressure and water vapor pressure at  $1473^{\circ}K$  for the system  $Cr_2O_3(s)-O_2(g)-H_2O(g)$ .

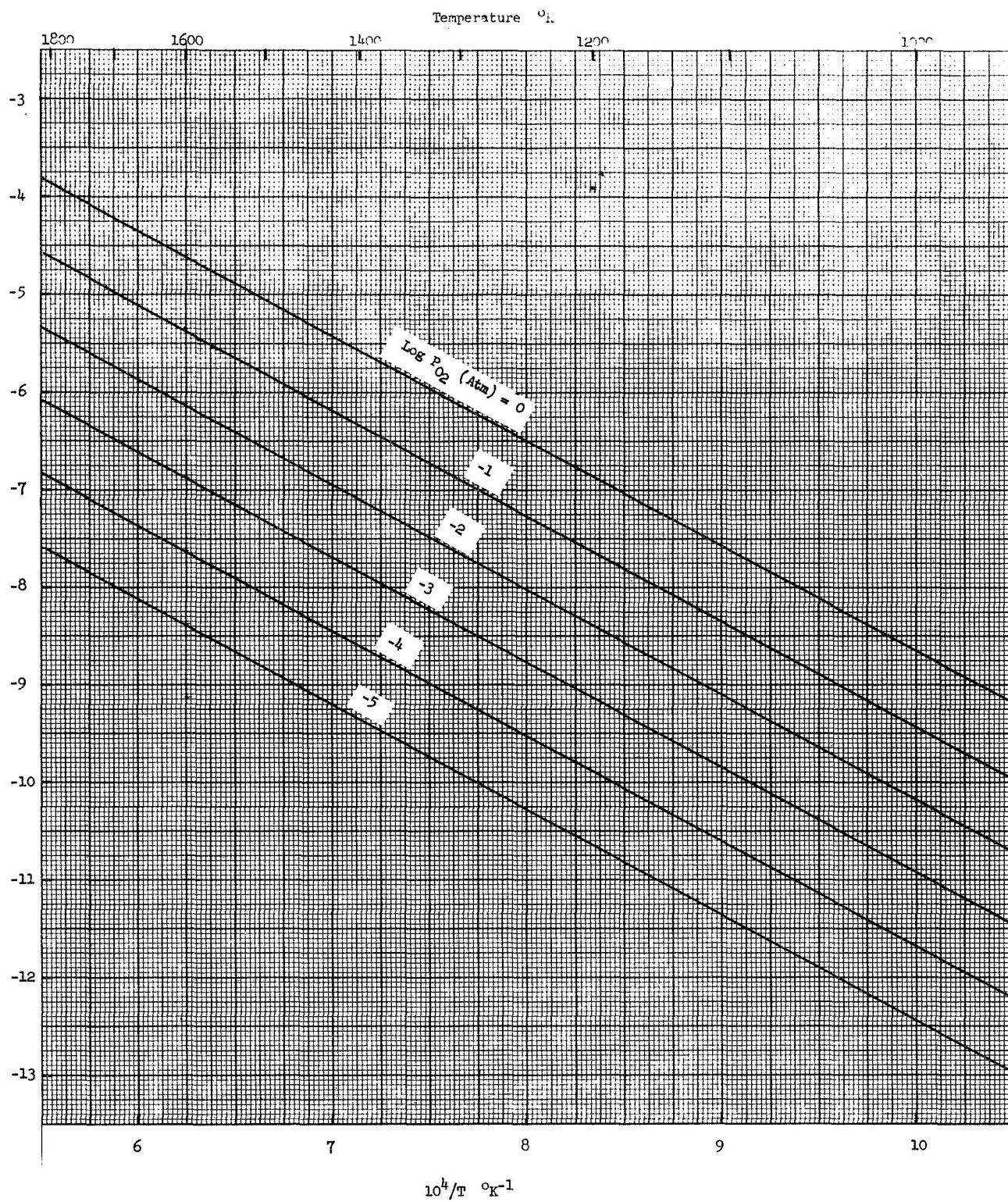


Fig. 16 Vapor pressures of  $\text{CrO}_3(\text{g})$  as a function of temperature and oxygen pressure for the Cr-O system.  
 $\text{Cr}_2\text{O}_3$  is the stable condensed phase.

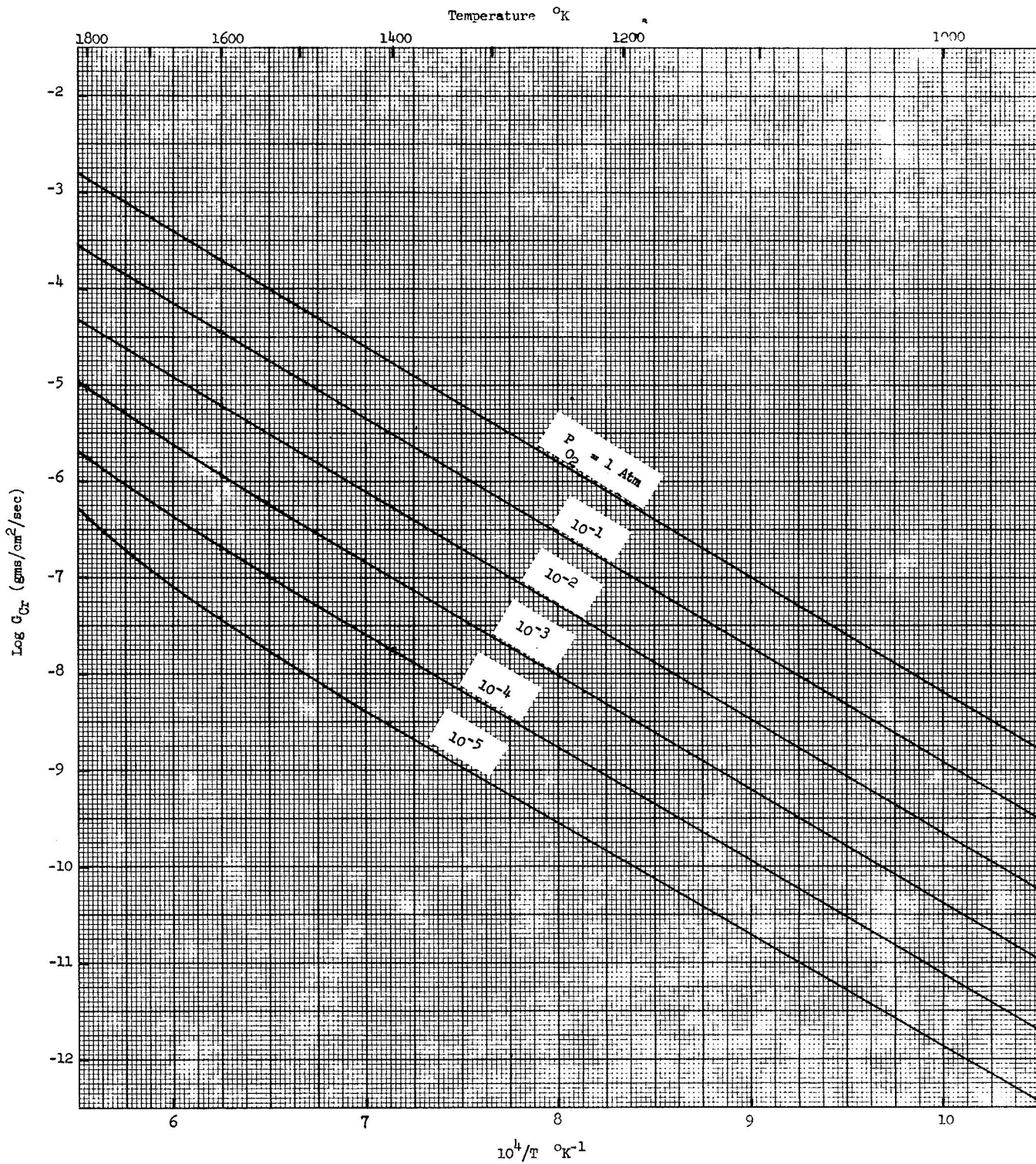


Fig. 17 Vaporization rate of Cr from oxidized TD-NiCr as a function of temperature and  $P_{O_2}$  (g).