# THERMODYNAMIC ACTIVITY OF CHROMIUM, VANADIUM OXIDE IN $CaO$-$SiO_2$-$MgO$-$Al_2O_3$ SLAGS

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## ABSTRACT

*Thermodynamic activities of chromium and vanadium oxide respectively containing in* $CaO$-$SiO_2$-$MgO$-$Al_2O_3$ *slags were measured in the present work using gas-slag equilibrium technique by well-defined oxygen partial pressures* ($10^{-3}$,$10^{-4}$,$10^{-5}$ *Pa*) *controlled by mixtures of CO,* $CO_2$ *and Ar gases at temperatures 1803,1823 K,1873,1923 K. The slags were kept in Pt crucibles during the equilibration the duration of which was 20 h. From a knowledge of the thermodynamic activity of Cr and vanadium in Cr(V)-Pt alloy, obtained from literature, and the oxygen partial pressure in the gas stream, it is possible to calculate the thermodynamic activity of chromium, vanadium oxide in the slag.*

*In view of the low Cr(V)-contents and the low oxygen potentials employed in the present studies, all the Cr in the slag was assumed to be present in the divalent state, which is in accordance with the observations of Forsbacka and Holappa. Analogously,* $VO_{1.5}$ *was considered as final phases in slag in vanadium systems. Activities of CrO showed a positive deviation from ideality but there is a strong negative deviation for VO1.5. Both of activities of CrO and* $VO_{1.5}$ *decreased with increasing of temperature. Mathematical correlations were developed for estimating contents of chromium and vanadium in slags as functions of the slag chemistry on the basis of the present results.*

***Key Words:*** *Thermodynamic activity, chromium oxide, vanadium oxide, equilibrium, slags.*

## INTRODUCTION

Chromium and vanadium are important alloying element in stainless steel. In order to control and minimize the oxidation of chromium and vanadium from the steel phase to the slag, it is necessary to have an understanding of the driving force for the oxidation reaction, a knowledge of the thermodynamic activities of chromium and vanadium in steel and those for chromium, vanadium oxide in the slag phase is important. The different valency states of chromium and vanadium oxide in slag are dependent on temperature, slag chemistry and oxygen partial pressure prevailing. However, there are a number of publications and it is particularly due to the high temperature and the lower oxygen partial pressure. Toker [1] investigated the phase relations and thermodynamics in Cr-O system. Villiers [2] studied the liquid-solidus relationship in the $CaO-CrO_x-SiO_2$ system using $CO_2/H_2$ gas mixtures keeping the oxygen partial pressure very low. The activity-composition relationship in the solid solutions has been determined by Tsai [3] and the activities of $CrO_x$ were reported to exhibit positive deviations from ideality. Besmann, Morita and other researchers [4, 5, 6, 7] studied the chromium oxide in slag. Pretorius et al. [8, 9] have investigated the oxidation of chromium in $CaO-SiO_2-CrO_X$ and $CaO-SiO_2-Al_2O_3-CrO_X$ systems. It was shown by these authors that the ratio of $Cr^{2+}/Cr^{3+}$ exhibited a tendency to decrease with the increase basicity of slag at the same oxygen partial pressure. Xiao *et al.* [10] also studied the same system by solid electrolyte galvanic cell and slag/metal equilibrium techniques. Pei [11] employed the slag/metal equilibration method under the desired oxygen partial pressure which was controlled by $H_2O/H_2$ gas mixtures. Farah [12] investigated the two redox equilibrium corresponding to $V^{3+}/V^{4+}$ and $V^{4+}/V^{5+}$ pairs in $CaO-SiO_2-Al_2O_3$ and $CaO-SiO_2-MgO$ melt. Distribution of vanadium in different valency states in slag has also been examined by other researchers [13, 14, 15, 16, 17]. Tsukihashi, *et al.* [18] investigated the effect of $Na_2O$ addition on the vanadium distribution between $CaO-CaF_2-SiO_2$ melts and carbon saturated iron. Inoue and Suito [19] investigated the distribution of vanadium between liquid iron and MgO saturated $CaO-SiO_2-MgO-FeO_x$ slag, which was increasing with the increasing of basicity of slag. Vermaak, *et al.* [20, 21, 22, 23, 24] studied the distribution of the vanadium and vanadium oxide between hot metal and slag.

In view of the differences in slag chemistry, temperature of the experiments and oxygen partial pressures imposed on the systems (which in turn, would influence the distribution of different valency states of vanadium in the slag) during the measurements, in the present work, the thermodynamic activity of chromium and vanadium oxide in slags with low chromium and vanadium contents was measured using the gas-slag equilibrium method at low oxygen partial pressures ($10^{-3}$,$10^{-4}$,$10^{-5}$ P) and different temperatures (1803, 1823 K, 1873, 1923 K).

## PRINCIPLE OF THE EXPERIMETNAL TECHNIQUE ADOPED

In the present experiments, very low oxygen partial pressures in the gas mixtures were used for the equilibration studies. Forsbacka and Holappa [25] have reported that, at low oxygen potentials, all Cr in the slag exists in the $Cr^{2+}$ state. Hence, in the present work, the presence of $Cr^{3+}$ in the slag was considered negligible. For slag including vanadium, vanadium exists as $V^{3+}$ state.

The equilibration reaction between the slag in the platinum crucible and the gas mixture can be represented as respectively:

$$Cr(Pt)_{(s)} + \frac{1}{2}O_{2(g)} = CrO_{(l)} \tag{1}$$

$$V(Pt)_{(s)} + \frac{3}{4}O_{2(g)} = VO_{1.5(s)} \tag{2}$$

The equilibrium constant, K can be represented as

$$K_1 = \frac{a_{CrO}}{a_{Cr} \cdot (P_{O_2})^{1/2}} = \exp\left(\frac{-\Delta G_1^{o}}{RT}\right) \tag{3}$$

$$K_2 = \frac{a_{VO_{1.5}}}{a_{\underline{V}} \cdot (P_{O_2})^{3/4}} = \exp\left(\frac{-\Delta G_2^{o}}{RT}\right) \tag{4}$$

Where *a* is the activities of the various species, K is the equilibrium constant and $\Delta G_i^o$ is the standard free energy of reaction. The $\Delta G_i^o$ of reactions were given by the expression:

$$\Delta G_1^o = -334218 + 63.81T\ (J) \tag{5}$$

$$\Delta G_2^o = -600405 + 112.97T\ (J) \tag{6}$$

# EXPERIMENT

## Raw Material

The raw materials used in this investigation are reagent-grade oxide powders. CaO, $Al_2O_3$ and MgO powders were heated at 1273 K for 12 hours in order to decompose the hydroxides and carbonates that might have been formed. $Cr_2O_3$ and $SiO_2$ powders were heated at 873 K for 8 hours in order to remove the moisture, $V_2O_3$ powder bought from Sigma Aldrich, Germany was kept in desiccator for use. The raw materials were mixed to obtain the targeted composition (total mass of each mixture was about 1.5~2 g) and ground thoroughly in an agate mortar and pressured into pellets with a diameter of 12 mm. Prepared samples were kept in a desiccator with silica gel as the desiccant ready for use.

## Experimental Set-up

A sketch of the furnace arrangement is presented in Figure 1. The experimental system consists of high temperature furnace equipment with a PID controlling program and with a Pt30 pct Rh/Pt6 pct Rh thermocouple as sensor. The slag samples were kept in platinum cups and were placed in an alumina crucible holder. A platinum spiral made of a wire of 0.5 mm diameter was placed inside the slag samples in order to minimize the sample losses due to creeping up of the slag along the crucible walls. The crucible holder was placed in the even-temperature zone of the furnace which was found, in an earlier calibration, to be about 100 mm. Special attention was paid to the gas inlet tube arrangement so that the gas mixture was delivered by a narrow alumina tube (inner diameter 4 mm) directly above the sample avoiding thermal segregation of the gases during the passage through temperature gradient in the furnace. The temperature of the sample was measured by a thermocouple placed close to the sample tray. Alumina runners were placed under the crucible holder in order to avoid breaking of the reaction tube by thermal shock during quenching the sample.

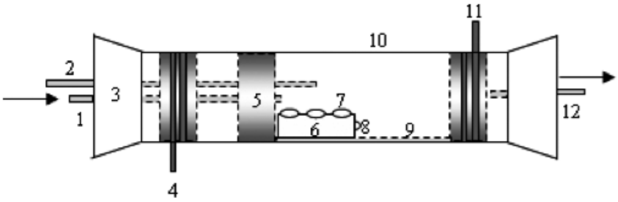


Figure 1: The sketch diagram of the experimental equipment. (1-gas inlet; 2-thermocouple; 3-silicon rubber stopper; 4-cooling water inlet; 5-refractory; 6-pure aluminum holder; 7-hole on the aluminum holder; 8-ceramic ring for pulling; 9-alumina runners; 10-reaction tube; 11-cooling water outlet; 12-gas outlet).

## Gas Cleaning System

In view of the extremely low oxygen partial pressures targeted in the present measurements, it was considered important to purify the gases used in the gas mixture carefully before introducing into the reaction tube. A gas cleaning system was used to further-purify the gases, *viz.* argon, carbon monoxide and carbon dioxide, high purity grade, supplied by AGA Stockholm. The gas cleaning train used in the present work is presented in Figure 2. Columns of silica gel, magnesium perchlorate and ascarite were used to remove the $H_2O$ and $CO_2$ in the gases. Columns of copper turnings at 823 K and magnesium chips at 773 K were used to remove the residual $O_2$ in the argon gas. Oxygen partial pressure in the outgoing gas was monitored continuously by using an oxygen sensor consisting of a $ZrO_2$-7.5 mol% CaO electrolyte tube kept at 973 K with a slow stream of dry air as the reference electrode. The oxygen partial pressure values measured were in agreement with those estimated by Thermo-Calc software for the desired composition of mixture gases employed.

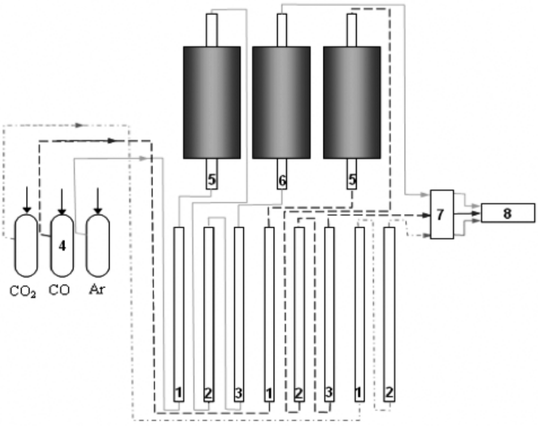


Figure 2: Gas cleaning system. (1-silica gel, 2-ascarite, 3-magnesium perchlorate, 4-bubbler, 5-copper turnings<823 K>, 6-magnesium chips<773 K>, 7-flow controller 8-gas mixture chamber)

## The Experimental Procedure

During the measurements, the furnace was heated to the desired temperature under argon gas at a flow rate of 200 ml per min. The furnace was kept at this temperature for at least one hour in order to ensure the attainment of constant value. The alumina holder with four platinum crucibles containing the slag samples was then introduced into the reaction tube and positioned in the even-temperature zone under flowing argon gas. Refractory radiation shields were positioned at both ends of the furnace in order to minimize heat loss. The reaction tube was closed using silicon rubber stoppers. The ends of the reaction tube were kept at 293 K by a water-cooling system. The mixture gas of CO, $CO_2$ and Ar mixed to the targeted ratio was introduced into the reaction tube. After the equilibration time, the alumina holder with the samples was quenched by quickly withdrawing the same to the cold end of the reaction tube under protection of argon gas. Samples were then taken out from platinum crucibles and stored in a desiccator for chemical analysis.

The slag samples were ground and were subjected to chemical analysis by X-ray fluorescence spectroscopy. All chemical analyses were performed by NILAB, Stockholm and the results were duly certified. As mentioned earlier, all the chromium in the slag was assumed to be present as $Cr^{2+}$ and vanadium as $V^{3+}$. The Pt wires from the spiral, embedded in the sample during the experiment as well as the Pt crucibles were also subjected to chemical analysis by atomic absorption spectroscopy. The Pt wire was also analyzed with respect to Si, Ca, Al and Mg apart from Pt and Cr, V. The contents of Al and Mg could not be monitored in this analysis as the amounts were below the detection limits. The contents of Si and Ca were found to be less than 0.1-wt%. The cross section platinum spiral wire was analyzed by SEM/EDS technique in order to ensure that the chromium dissolved in the platinum was uniformly distributed.

## RESULTS AND DISCUSS

### Equilibrium Time

The equilibrium time between the mixture gases with slag system and the binary alloy need to be confirmed before the actual measurements were started. A mixture of $CaO\text{-}SiO_2\text{-}MgO\text{-}Al_2O_3\text{-}CrO_X$ system was equilibrated with pure Pt crucible (99.99%) for various length of time (6, 8, 12, 15, 20 h) and the samples were analyzed after furnace-quenching. the relationship between content of chromium in Pt crucible as function of soaking time was plotted in Figure 3. when soaking time is more than 15 hours, the content of chromium are likely keep constant, In the present work, an equilibration time of 20 hours was chosen for all the experiments. The cross section of each quenched crucibles was analyzed by SEM-EDS technique. The result of line analysis of cross section of platinum crucible which kept chromium and vanadium oxide slags for 20 h is seen in Figure 4 that there is no concentration gradient across the thickness of the crucible. Thus, chromium concentration throughout the crucible is uniform confirming the attainment of equilibrium between the Pt and the slag phase as well.

### Activity and Activity Coefficient of Chromium and Vanadium in Cr(V)-Pt Alloy

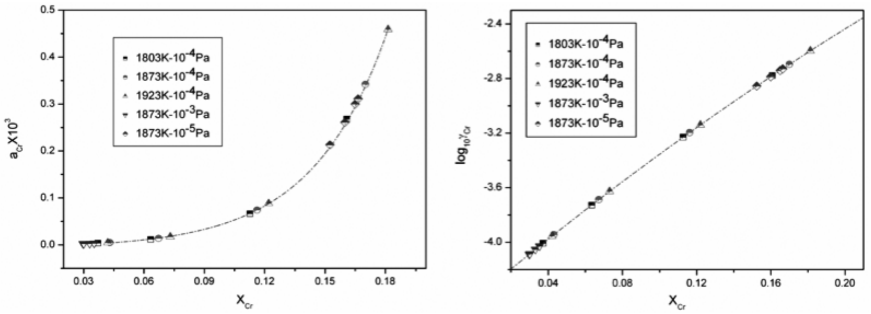
To the knowledge of the present authors, the relationship between activity coefficient and atomic fraction of chromium, vanadium in Cr(V)-Pt alloys has earlier been proposed by Pretorius [8]. This is given in Equation, *viz*.

$$\log_{10} \gamma_{Cr} = -4.42 + 11.39X_{Cr} - 7.35X_{Cr}^{2} \tag{7}$$

$$\log_{10} \gamma_{V} = -6.72 + 17.66X_{V} - 13.33X_{V}^{2} \tag{8}$$

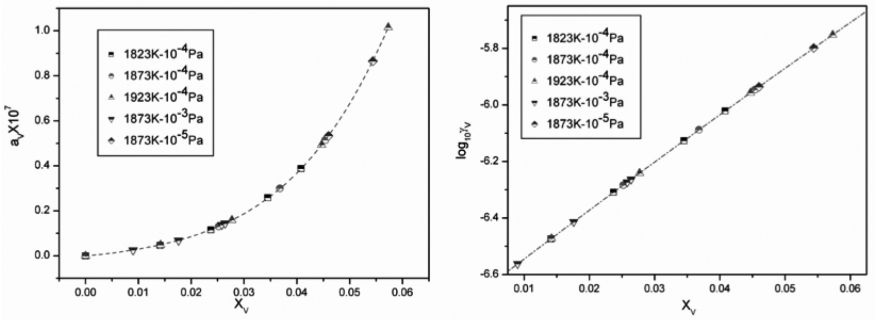
Plots of the activity of chromium, vanadium as a function of $X_{Cr}$, $X_V$ in accordance with Equation 3 and 4 are presented in Figure 5(a) and in Figure 6(a). Both of activities of chromium, vanadium exhibit a strong negative deviation from ideality when the content of chromium and vanadium are very small. At higher contents, there is a tendency for a changeover to positive deviations from Raoult's law.

The logarithm of activity coefficient of chromium, vanadium were calculated based on Equation 7 and 8 corresponding to the vanadium contents in Cr(V)-Pt alloy. As can be seen in Figure 5(b) and Figure 6(b) respectively, the logarithm of activity coefficient of chromium, vanadium increases with increasing of content of chromium, vanadium in Cr(V)-Pt alloy.



(a) (b)

Figure 5: Activity and Logarithm of activity coefficient ($Log_{10}r_{Cr}$) of chromium as a function of chromium content in Cr-Pt alloy($P_{02}$=$10^{-3}$, $10^{-4}$, $10^{-5}$ Pa; T=1803, 1873, 1923 K)
Pure solid Cr as the standard state

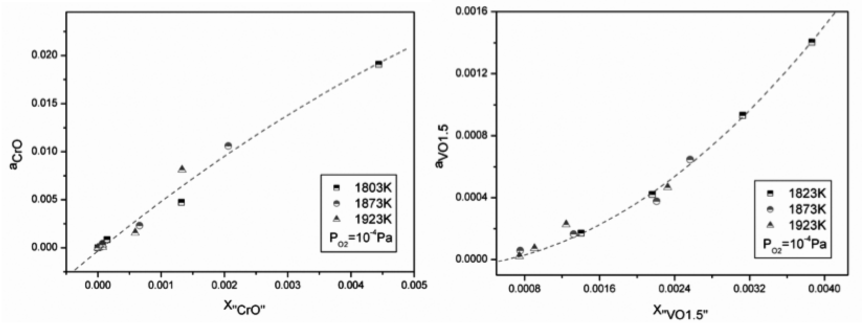


(a) (b)

Figure 6: Activity and Logarithm of activity coefficient ($Log_{10}r_V$)of vanadium as a function of vanadium content in V-Pt alloy($P_{02}$ = $10^{-3}$,$10^{-4}$, $10^{-5}$ Pa;T=1823,1873,1923 K)
Pure solid V as the standard state

## Effect of Content of Chromium, Vanadium Oxide on Activity of Chromium Vanadium Oxide

Because of the low content of chromium, vanadium oxide in final slag, it is difficult to analyze the exactly the valence of chromium, vanadium in slag. The activities of chromium, vanadium oxide with bivalent chromium and trivalent vanadium plotted as a function of mole fraction of chromium, vanadium oxide in slag was presented in Figure 7. The activity of CrO has a positive deviation from ideality in the present composition range with increasing of temperature. These results are in agreement with those reported by Xiao, *et al.* [10]. The activity-composition relationship for vanadium system shows a strong negative deviation from ideality, it can be seen in Figure 7(b).



(a) (b)

Figure 7: Thermodynamic activity of chromium (CrO), vanadium oxide ($VO_{1.5}$) as a function of mole fraction of CrO and $VO_{1.5}$ in slag ($PO_2=10^{-4}$ Pa) ((a):1803, 1873 and 1923 K; (b):1823, 1873 and 1923 K)

## Model for the Content of Chromium, Vanadium in Alloy and Slag Respectively

The general expression for the chromium–reduction reaction (Equation 9) under low oxygen partial pressure was developed in the present work. The expression is similar to those derived in the case of sulfide capacity data for slags found in earlier literature [27, 28, 29].

$$CrO_x(slag) = [Cr]_{Pt} + \frac{x}{2}O_2(g) \tag{9}$$

The equilibrium constant of Equation 9 can be expressed as:

$$K_9 = \frac{a_{[Cr]} \cdot (P_{O2})^{\frac{x}{2}}}{a(CrO_x)}$$

Based on the express, if the following parameters were assumed that:

- Henrys law is applicable to the activity coefficient of chromium in the Cr-Pt alloy in the range of concentration studied in the present work
- The activity coefficient of chromium oxide is also constant
- The effect of temperature, oxygen partial pressure and slag basicity are to be considered.

The expression for the weight percent chromium in slag for a given activity of Cr in metal phase is:

$$\log_{10}(\%Cr)_{slag} = a + \frac{b}{T} + c\log_{10}(a_{Cr}) + d\log_{10}(P_{O2}) + e\log_{10}B$$

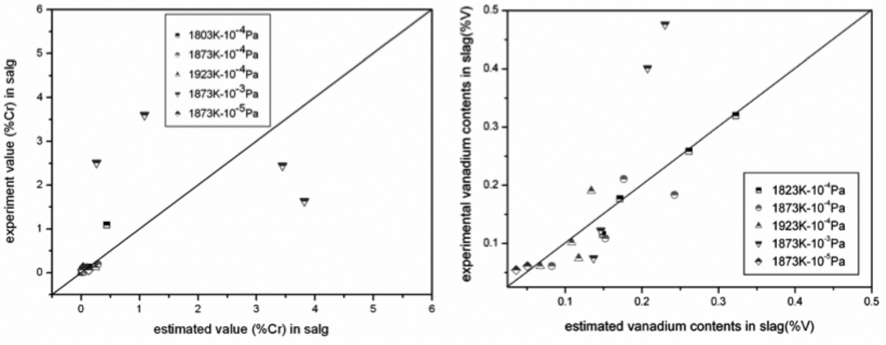
- Where *a*, *b*, *c*, *d* and *e* are constant
- T is the experiment equilibrium temperature
- $(\%Cr)_{slag}$ represents the weight percent chromium in slag
- $a_{Cr}$ represents the activity of chromium in alloy
- $P_{O2}$ represents equilibrium oxygen partial pressure.
- B represents the basicity of slag ( $B = \frac{wt\%CaO + wt\%MgO}{wt\%SiO_2 + wt\%Al_2O_3}$ )

The same rules were defined for vanadium system. All of the constants in expression were evaluated using the present results and the equation in the final form is follows:

$$\log_{10} (\%Cr)_{slag} = 1.31 + \frac{12481}{T} + 0.84 \text{ x } \log_{10} (a_{Cr}) + 1.59 \text{ x } \log_{10}(P_{O2}) - 6.77 \text{ x } \log_{10} B$$

$$\log_{10} (\%V)_{slag} = -5.61 + \frac{11825}{T} + 0.28 \text{ x } \log_{10} (a_{V}) + 0.46 \text{ x } \log_{10}(P_{O2}) - 2.45 \text{ x } \log_{10} B$$

The estimated and experimental content of chromium in slag are plotted in Figure 8(a). Most of the experimental points are in agreement with each other except the samples under the oxygen partial pressure of $10^{-3}$ Pa. This indicates that the oxygen partial pressure $P_{O2}=10^{-3}$ Pa might have a strong influence on the behavior of chromium and the effect of the presence of $Cr^{3+}$ may be significant. The relation between estimated and actual content of vanadium in slag shows reasonably good agreement as can be seen in Figure 8(b). The deviation in the case of the two experimental points corresponding to $P_{O2}=10^{-3}$ Pa is likely to be due to the formation of higher valence states of vanadium in this case.



(a) (b)

Figure 8: Estimated and experimental content of chromium and vanadium in slag

## CONCLUSIONS

- The activities of CrO and $VO_{1.5}$ in some $CaO$-$SiO_2$-$MgO$-$Al_2O_3$ slags were determined by equilibration with a gas phase with a well-defined partial pressure of oxygen.
- Activity of chromium, vanadium in Cr(V)-Pt represent strong negative deviation from ideality. And the logarithms of activity coefficient of chromium, vanadium are increasing with increasing of temperature.
- Activity of CrO represents positive deviation from ideality, but that is a strong negative deviation for $VO_{1.5}$.
- A relationship for estimating the actual content of chromium, vanadium in slag as a function of chromium in the molten metal phase were developed from the present results, *viz*.

The agreement between the values obtained by the above equation and the experimental results is satisfactory, especially at lower oxygen partial pressures used.

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