# Communication

## Some Thermodynamic Aspects of the Oxides of Chromium

AYUSH MITTAL, GALINA JELKINA ALBERTSSON, GOVIND SHARAN GUPTA, SESHADRI SEETHARAMAN, and SANKARAN SUBRAMANIAN

To understand Cr emissions from slag melts to a vapor phase, an assessment of the stabilities of the chromium oxides at high temperatures has been carried out. The objective of the present study is to present a set of consistent data corresponding to the thermodynamic properties of the oxides of chromium, with special reference to the emission of hexavalent chromium from slags. In the current work, critical analysis of the experimental data available and a third analysis in the case of $Cr_2O_3$ have been carried out. Commercial databases, Fact Sage and ThermoCalc along with NIST-JANAF Thermochemical Tables, have been used for the analysis and comparisons of the results that are presented. The significant discrepancies in the available data have been pointed out. The data from NIST-JANAF Thermochemical Tables have been found to provide a set of consistent data for the various chromium oxides. An Ellingham diagram and the equations for the $\Delta G°$ (standard Gibbs free energy change) of formation of $CrO_x$ have been proposed. The present analysis shows that $CrO_3(g)$ is likely to be emitted from slag melts at high oxygen partial pressures.

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Chromium is an important alloying element in stainless steelmaking. During the production of chromium-containing steels, the resultant slag can contain as much as 8 mass pct Cr. As a result of the extremely carcinogenic nature of hexavalent chromium, serious efforts are made so that chromium is stabilized in the slag and does not get leached out by acid rains. On the other hand, little is known regarding the emission of the oxide of chromium during the tapping of the slag at steelmaking temperatures. A recent publication[1] has pointed out the risk of Cr-emission from slags at high temperatures under high oxygen potentials. Such emissions may also occur if chromite refractories are exposed to air at high temperatures. While the emission of Cr as a gaseous oxide could be confirmed in this work,[1] the nature of the oxide phase emitted as to whether it was hexavalent chromium is not clear. Because of the importance of the system Cr–O in stainless steel processing as well as of Cr-emissions at high temperatures, the present work was taken up to examine the stabilities of various oxides of chromium.

Current work presents the data corresponding to the thermodynamic properties of the oxides of chromium, with emphasis on the emission of hexavalent chromium from slags. Critical analysis of the experimental data available with emphasis on self-consistency, third law analysis, where it is possible and comparisons have been carried out. The current article addresses an important question; *viz.* which oxide is emitted when chromium slags are heated in an oxidizing atmosphere at steelmaking temperatures. The alloy steel industries in Sweden have already expressed concern with respect to the emission of $Cr^{6+}$.

Some of the present authors have carried out experimental investigations with respect to the thermodynamics of chromium-containing slags.[1–6] Among these, the publication on the studies on the vaporization of chromium from thin slag films at steelmaking temperatures in oxidizing atmosphere[1] is significant as these results indicated that chromium loss increased with increase in temperature and oxygen partial pressure.

A study[2] of the thermodynamic activity of chromium oxide in $CaO–SiO_2–MgO–Al_2O_3–CrO_x$ slags at elevated temperatures and oxygen partial pressures in the range of $10^{-5}$–$10^{-3}$ Pa has shown that the activities of CrO have a strong positive deviation from ideality and decrease with increasing temperature and oxygen partial pressure. Albertsson *et al.*[5,6] conducted a series of studies of the system $CaO–MgO–SiO_2–Cr_2O_3–(Al_2O_3)$ at elevated temperatures and different oxygen partial pressures. It has been shown that oxygen partial pressure has a strong impact on the chromium partition in slags, as a result of the presence of $Cr^{6+}$ in the slag at higher oxygen partial pressures.

Chromium is reported to exhibit valence states +1, +2, +3, +4, and +6 in combination with oxygen, *viz.* $Cr_2O$, CrO, $Cr_2O_3$, $CrO_2$, and $CrO_3$. Of these, very little is known about $Cr_2O$, even though it has been mentioned in commercial databases like FactSage Software (FactSage 6.1)-Thermfact Ltd (Montreal, Canada) and GTT-technologies (Aachen, Germany).[7] Important publications that form the basis for FactSage evaluations of condensed phases especially at high temperatures are those by Degterov and Pelton.[8–10] Databases chosen were Fact53 and FToxid. FactSage also considers

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AYUSH MITTAL, Bachelor of Technology (B.Tech) Student, is with the Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Roorkee 247 667, India, and also with the Department of Materials Engineering, Indian Institute of Science, Bangalore 560 012, India. GALINA JELKINA ALBERTSSON, formerly PhD Student and is now Doctor of Philosophy, with the Department of Materials Science and Engineering, Royal Institute of Technology, 100 44 Stockholm, Sweden. Contact e-mail: galinaa@kth.se GOVIND SHARAN GUPTA, Professor, is with Department of Materials Engineering, Indian Institute of Science. SESHADRI SEETHARAMAN, formerly Visiting Professor with the Department of Materials Engineering, Indian Institute of Science, and is now Professor Emeritus with the Department of Materials Science and Engineering, Royal Institute of Technology. SANKARAN SUBRAMANIAN, Professor, is with the Department of Materials Engineering, Indian Institute of Science.

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the compilations of Barin *et al.*[11] Another commercial software selected in the present assessment was ThermoCalc[12] software (The Royal Institute of Technology, Stockholm, Sweden). The authors cannot retrieve the sources of the original experimental data used for the assessment in this database. The intention of comparing the commercial databases is because these present assessed, critically reviewed data often by expert panels like Scientific Group Thermodata Europe (SGTE), and thus, a total reassessment from raw data in the present work is considered redundant.

The oxides $CrO_2$ and $CrO_3$ are both low melting oxides. The oxide $CrO_2$ has been reported to decompose above its melting point. Kubota[13] reported that $CrO_2$ has a decomposition temperature of 823 K (550 °C), whereas Darnell and Cloud[14] claimed that decomposition occurs just above 523 K (250 °C). On the other hand, a stability diagram extracted from FactSage indicates $CrO_2$ as a solid phase at steelmaking temperatures as shown in Figure 1.

This can be compared with the phase diagram extracted from ThermoCalc,[12] presented in Figure 2, which is quite similar to the phase diagram presented earlier by Muan.[15] In this figure, the gas phase is not represented. It is shown in this diagram that $CrO_2$ solid does not exist even at high oxygen potentials.

Among the oxides of chromium, $CrO_3$ is reported to have the lowest melting point, 470 K (197 °C). The boiling point of $CrO_3$ is 524 K (251 °C). Furthermore, the relative stabilities of $CrO_2$ and $CrO_3$ have not been ascertained and there is no mention of $CrO_3$ in any Cr–O phase diagram.

Morita *et al.*,[16,17] in their studies on slags containing chromium oxides, reported that at high oxygen potentials, a significant amount of Cr exists as $Cr^{6+}$. Mausbach *et al.*[18] had investigated the slag systems using a spectroscopic technique in the ultraviolet–visible region and reported the presence of $Cr^{6+}$. This was confirmed by Okretic *et al.*[19] who employed the same technique.

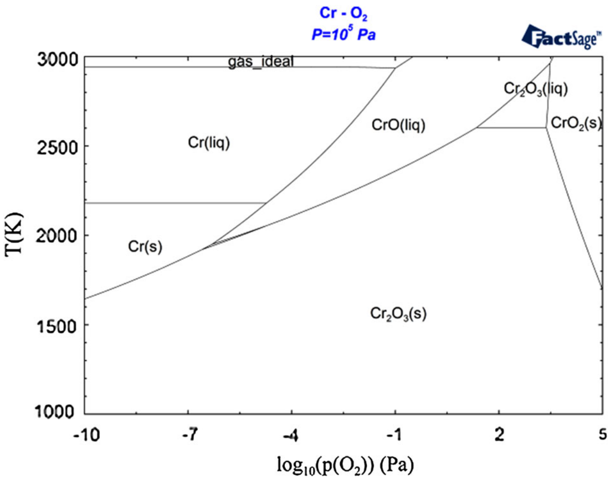

Fig. 1— Phase stability diagram of the system $Cr–O_2$ as a function of oxygen pressure in the temperature range 1000 K to 3000 K (727 °C to 2727 °C).[7]

If $CrO_2$ and $CrO_3$ melt at low temperatures, they should have high vapor pressures at elevated temperatures. The existence of $CrO_2$ vapor would be contradictory to the earlier observations of decomposition of this compound.[13,14] Okretic *et al.*[19] estimated the vapor pressure of $CrO_3$ as 0.1 Pa at 1773 K (1500 °C). On the other hand, the vapor pressure of $CrO_3$ according to FactSage, which seems to be more realistic, is presented in Figure 3.

An assessment of the gas phase chromium species was reported earlier by Ebbinghaus.[20] In this compilation, the author used the data for CrO(g), $CrO_2$(g), and $CrO_3$(g) provided by Glushko *et al.*[21] It is pointed out that the compilation of Glushko *et al.*[21] includes the electronic and vibration spectra corresponding to the oxides of Cr. On the other hand, JANAF compilations provide the data for condensed and gaseous phases that are found to be mutually consistent. This would facilitate establishing compatibility between both condensed as well as gas species. In the present work, JANAF tables[22] are considered, along with FactSage and ThermoCalc,[12] as sources for the thermodynamic data involving species containing chromium and oxygen, with relevance to chromium emissions from condensed phases.

Any thermodynamic assessment needs to consider the synthesis and characterization conditions for the oxide compound. The present approach is to consider reliable raw data available in literature and compare the same with three sources that provide data, *viz.* JANAF thermochemical tables,[22] FactSage,[7] and ThermoCalc.[12] In some cases, where the raw data are available, these have been considered. The present assessment is confined to the pure oxides.

In the case of calculating the standard Gibbs energies of formation, $\Delta G^{\circ}_{f}$, of the various oxides from the pure elements, the reaction

$$2x\ \mathrm{Cr(s)} + \mathrm{O_2(g)} = 2\ \mathrm{Cr}_x\mathrm{O}(\mathrm{s}, l\ \mathrm{or\ g}) \qquad [1]$$

is always considered for 1 mol of oxygen. As the thermodynamic data for pure chromium metal (solid) have been well assessed in the sorces,[7,12,22] and oxygen is pure gas at 101325 Pa, these estimations can be made if the thermodynamic data are available for the oxide phase. A good coverage of the earlier literature on their thermodynamic parameters can be found in the publication of Chase.[23]

*$Cr_2O$*: Very little information is available regarding the formation of this suboxide. Considering the similarity with $Al_2O$, it can only be surmised that this compound may be stable at very low oxygen pressures and under high vacuum. The present authors only find its existence in Westdorp,[24] who suggested its formation at 2273 K (2000 °C). FactSage,[7] ThermoCalc,[12] and JANAF[22] do not have this compound in their compilations, and there is no value for the standard Gibbs free energy of formation, $\Delta G^{\circ}_{f(2)}$, available for the reaction

$$4\ \mathrm{Cr(s)} + \mathrm{O_2(g)} = 2\ \mathrm{Cr_2O(g)}. \qquad [2]$$

*CrO*: The XRD-PDF (X-ray diffraction—powder diffraction file) card corresponding to this compound[25] provides the X-ray crystallographic data with the

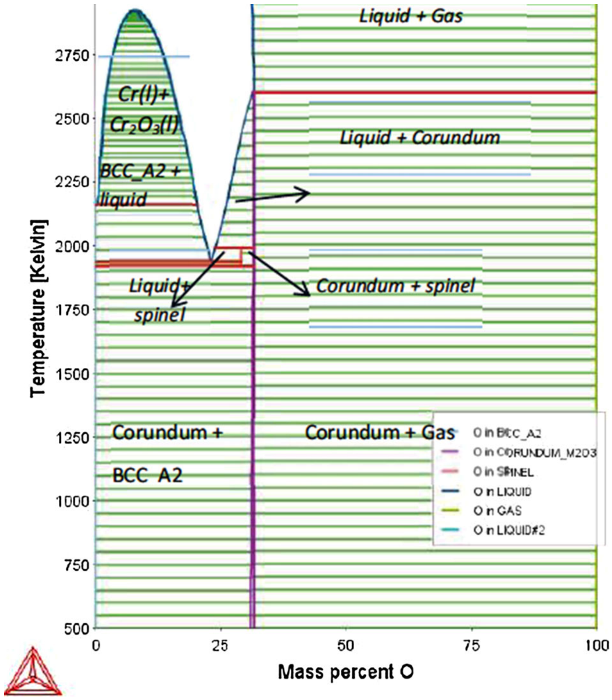

Fig. 2— The Cr–O diagram from ThermoCalc.[12]

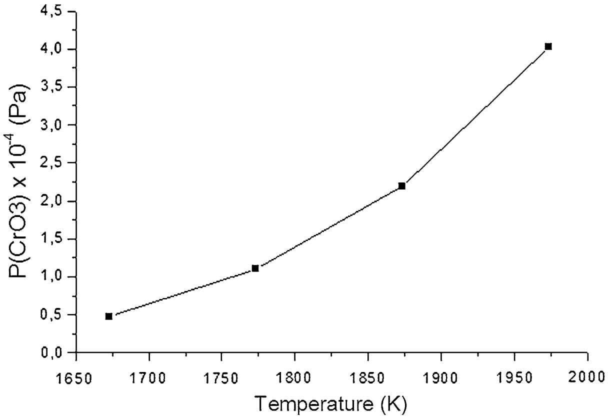

Fig. 3— The partial pressure of $CrO_3$(g) (Pa) as a function of temperature in Cr–$O_2$ system at elevated temperatures.[7] The partial pressure of $O_2$(g) = $9 \times 10^4$ Pa.

original source from Lux and Proeschel.[26] It is stated[26] that CrO will be formed if $Cr_2O_3$ is heated at 1323 K (1050 °C) in nitrogen–hydrogen atmosphere. The formation reaction for CrO(g) from the elements is represented as

$$2\ \mathrm{Cr}\ (s) + \mathrm{O_2}(g) = 2\ \mathrm{CrO}\ (g). \qquad [3]$$

The Gibbs energy of formation for this reaction, $\Delta G^{\circ}_{f(3)}$, can be retrieved from all three sources, and these are plotted as functions of temperature in Figure 4.

FactSage, ThermoCalc, and JANAF all show the formation of CrO in gaseous phase, and there is no solid or liquid CrO formation taking place. The $\Delta G^{\circ}_{f(3)}$ from all three sources show negative slopes with temperature in accordance with the Second Law of Thermodynamics.

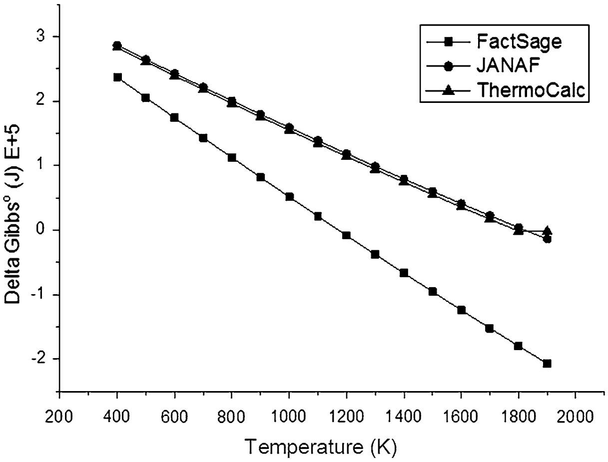

Fig. 4— The standard Gibbs energy of formation of CrO, $\Delta G^{\circ}_{f(3)}$ as a function of temperature from three different sources.[7,12,22]

FactSage[7] shows that the compound CrO is stable above 1100 K (827 °C) as shown in Figure 4. JANAF[22] and ThermoCalc[12] data clearly show that CrO is unstable below 1813 K (1530 °C). The differences are inexplicable. It is, however, interesting to note that, in slag systems, $Cr^{2+}$ has been reported to be stable at low oxygen potentials and low basicities.[3] With increase of oxygen potential and basicity, the higher valence state $Cr^{3+}$ is reported[3] to be stabilized. A good coverage of the earlier literature on the thermodynamic parameters of CrO can be found in the publication of Chase.[23] This work reports the results of calorimetric measurements of the molar heat capacity, $C_p$, for CrO (g) up to 6000 K (5727 °C). Figure 5 shows the $C_p$ molar heat capacity (CrO,g) from JANAF[22] based on the results reported by Chase[23] in the temperature range 400 K to 1900 K (127 °C to 1627 °C).

*$Cr_2O_3$*: $Cr_2O_3$ is the most stable oxide of chromium and has a melting point of 2708 K (2435 °C). This oxide has been experimentally studied extensively. The XRD data are provided in the XRD-PDF database[27] and by Ohyama and Kishida.[28] A good coverage of the earlier literature on the thermodynamic parameters of $Cr_2O_3$ can be found in the publication of Gurevich *et al.*[29] These authors have carried out calorimetric measurements of the molar heat capacity, $C_p$, for $Cr_2O_3$ (s) up to 480 K (207 °C). The thermodynamic functions for $Cr_2O_3$ by the extrapolation of the data up to 1800 K (1527 °C) have been proposed by these authors. The $C_p$ values of $Cr_2O_3$ as a function of temperature from this work are compared with the data from FactSage,[7] ThermoCalc,[12] and JANAF[22] in Figure 6.

There is a general agreement among the values from different sources with the JANAF line almost superimposed on the results of Gurevich *et al.*,[29] suggesting that JANAF values are based on these results. This was confirmed by the present author in a third law analysis.

The Gibbs free energy for the formation of $Cr_2O_3$ (s), $\Delta G^{\circ}_{f(4)}$ corresponding to the reaction

$$4/3\mathrm{Cr}(s) + \mathrm{O_2}(g) = 2/3\mathrm{Cr_2O_3}(s) \qquad [4]$$

according to the three data sources[7,12,22] are presented in Figure 7.

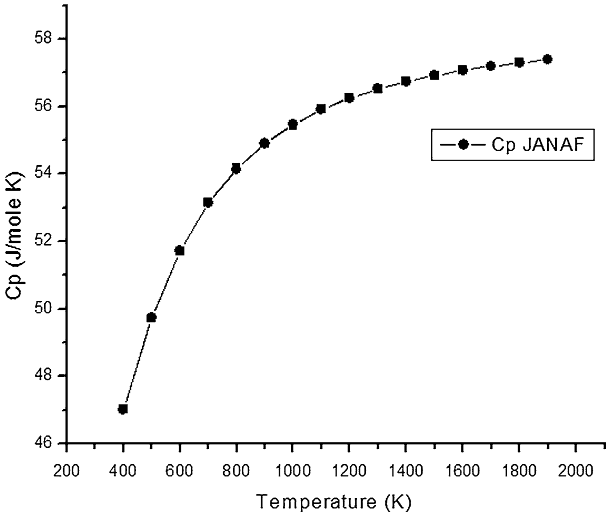

Fig. 5— Recommended curve of $C_p$ (CrO,g) from JANAF[22] based on the results reported by Chase[23] for temperature range of 400 K to 1900 K (127 °C to 1627 °C).

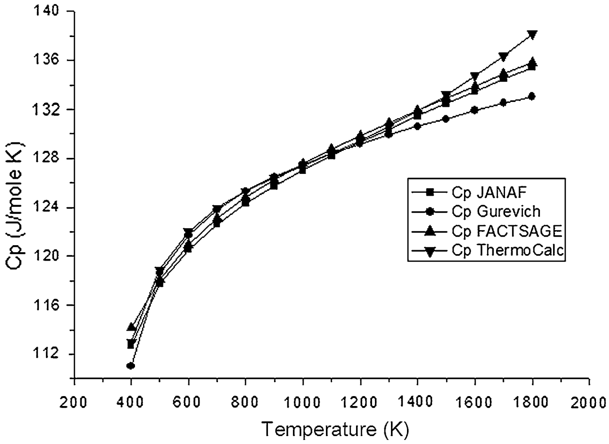

Fig. 6— A comparison of $C_p$ ($Cr_2O_3$, s) from Gurevich *et al.*[29] and JANAF,[22] FactSage,[7] and ThermoCalc.[12]

Reaction [4] with a reactant gas phase leading to a product in the condensed phase should lead to a decrease in entropy or increase in $\Delta G^{\circ}_{f(4)}$ as a function of temperature, which is valid in the compilation of all three data sources.[7,12,22]

*$CrO_2$*: The XRD pattern is provided in the XRD database.[30] Singh *et al.,*[31] from thermal analysis experiments, report that this compound is not stable under ambient oxygen partial pressure above 550 K (277 °C) decomposing to the more stable $Cr_2O_3$ corroborating earlier literature. These authors also provide the HXRD (high-pressure X-ray diffraction) patterns for $CrO_2$. DeVries[32] and Rodbell and DeVries[33] examined the decomposition of $CrO_2$ to $Cr_2O_3$, the latter under high pressure.

The Gibbs free energy of formation for $CrO_2$, $\Delta G^{\circ}_{f(5)}$ corresponding to the reaction

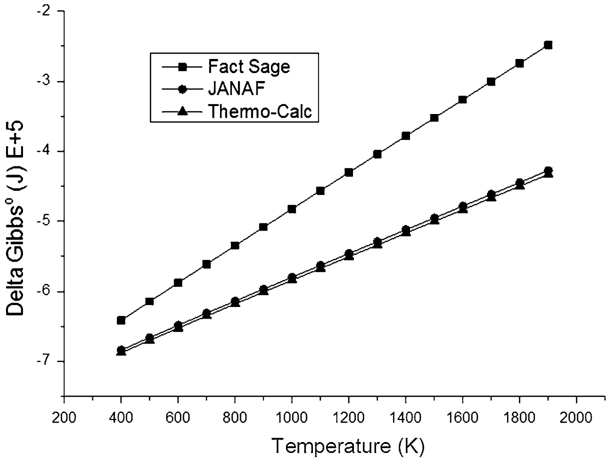

Fig. 7—The $\Delta G^{\circ}_{f(4)}$ plot for Reaction [4] from different data sources.[7,12,22]

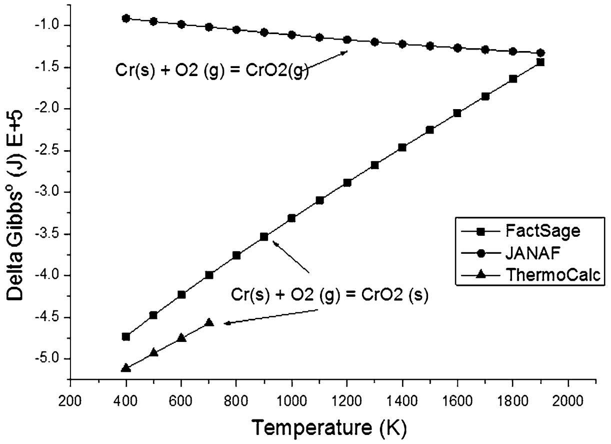

Fig. 8—The $\Delta G^{\circ}_{f(5)}$ plot for Reaction [5][7,12] and Reaction [6].[22]

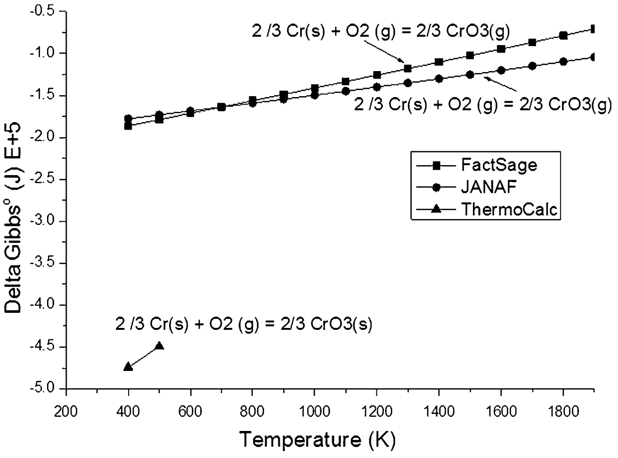

Fig. 9—The $\Delta G^{\circ}_{f(7)}$ plot for Reaction [7] from different data sources.[7,12,22]

$$Cr(s) + O_2(g) = CrO_2(s) \qquad [5]$$

has been presented by FactSage[7] and ThermoCalc,[12] and these values are compared in Figure 8.

Both FactSage and ThermoCalc show strong positive slopes for Reaction [5] indicating that the stability of the compound decreases as the temperature is increased. It should also be noted that ThermoCalc[12] gives data for $CrO_2$ only up to 700 K (427 °C) and that there is no liquid or gaseous $CrO_2$ phase present in the ThermoCalc or FactSage databases for the temperature range 400 K to 1900 K (127 °C to 1627 °C), whereas JANAF[22] gives the formation for only the gaseous phase.

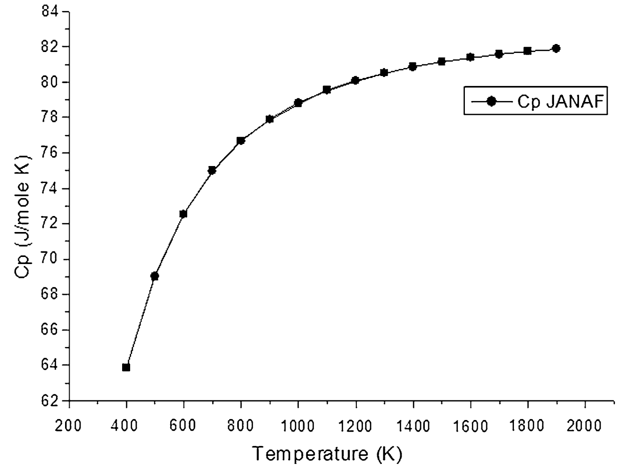

Fig. 10—$C_p$ (molar heat capacity) ($CrO_3$, g) from JANAF[22] by Chase[23] for a range of 400 K to 1900 K (127 °C to 1627 °C).

In the case of Reaction [6]

$$Cr(s) + O_2(g) = CrO_2(g) \qquad [6]$$

the only values available are from JANAF. The $C_p$ values of $CrO_2$ have been reported by Chase[23] even for higher temperatures. This apparently contradicts the decomposition results reported earlier.[13,14] Relying on the data presented by JANAF,[22] the $\Delta G^{\circ}_{f(6)}$ for Reaction [6] is presented in Figure 8.

It is shown that the $\Delta G^{\circ}_{f(6)}$ values are near zero according to JANAF with a slight negative slope with increase of temperature. The near-zero $\Delta G^{\circ}_{f(6)}$ values for Reaction [6] as reported by JANAF[22] may perhaps explain the earlier observations of the decomposition of $CrO_2$.

*$CrO_3$*: The XRD data and Raman spectroscopy results provided by Richter and Öhlmann[34] show the formation of $CrO_3$ by the calcination of chromic acid solution impregnated on silica. During this process, chromic acid would be decomposed to $\alpha$-$Cr_2O_3$. The $\Delta G^{\circ}_{f(7)}$ plot for $CrO_3$ corresponding to the Reaction [7], *viz.*

$$2/3\ Cr(s) + O_2(g) = 2/3\ CrO_3(g) \qquad [7]$$

from the three sources[7,12,22] are presented in Figure 9.

FactSage and JANAF present the data for the gaseous phase only, whereas ThermoCalc shows only the formation of the solid phase. So the JANAF and FactSage values should not be compared with ThermoCalc.

As the number of gas molecules decreases as a result of the reaction, the Gibbs free energy of formation for Reaction [7] $\Delta G^{\circ}_{f(7)}$ is expected to have a positive slope

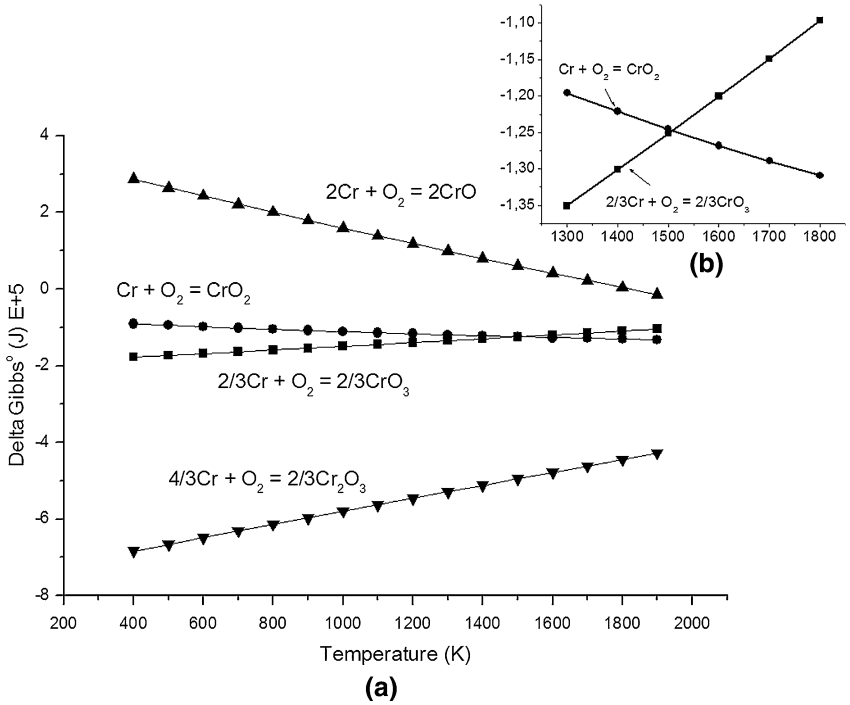

Fig. 11— (*a*) The Ellingham diagram for the oxides of chromium with data from JANAF.[22] (*b*) The enlarged view of crossing of the lines for $CrO_2$(g) and $CrO_3$ (g).

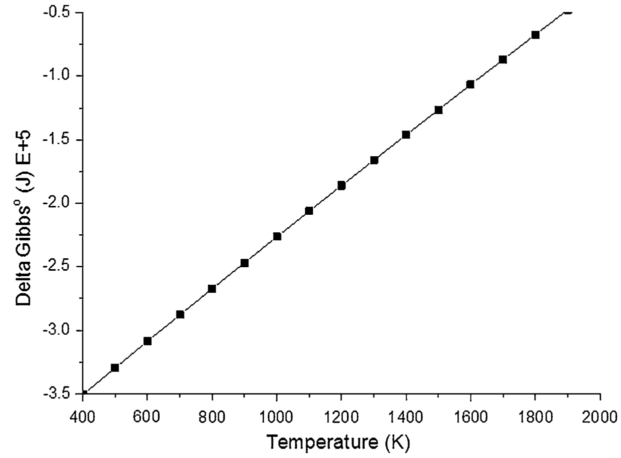

Fig. 12—$\Delta G°$ for Reaction [2] $CrO_2$ (g) + $O_2$ (g) = 2 $CrO_3$ (g).

**Table I. Equations for the $\Delta G_f^\circ$**

| Reaction | $(A + BT) \times 10^5$ (J) |
|---|---|
| $2Cr(s) + O_2(g) = 2CrO(g)$ | 3.618 – 0.002T |
| $4/3Cr(s) + O_2(g) = 2/3Cr_2O_3(s)$ | −7.503 + 0.0017T |
| $Cr(s) + O_2(g) = CrO_2$ (g) | −0.824 – 0.0003T |
| $2/3Cr(s) + O_2(g) = 2/3CrO_3(g)$ | −1.98 + 0.0005T |

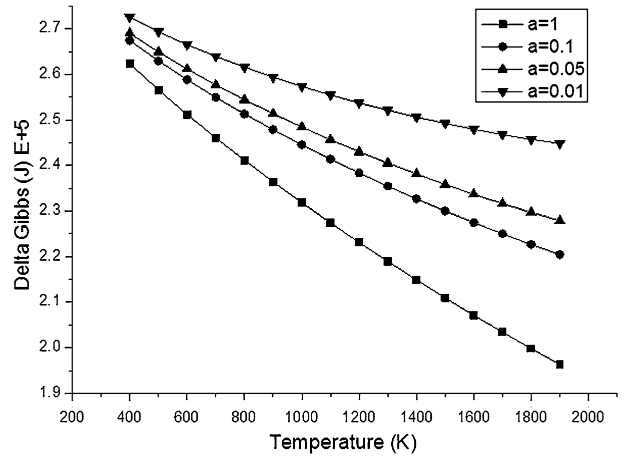

Fig. 13— The $\Delta G_8$ plot for Reaction [9] at different $Cr_2O_3$ activities.

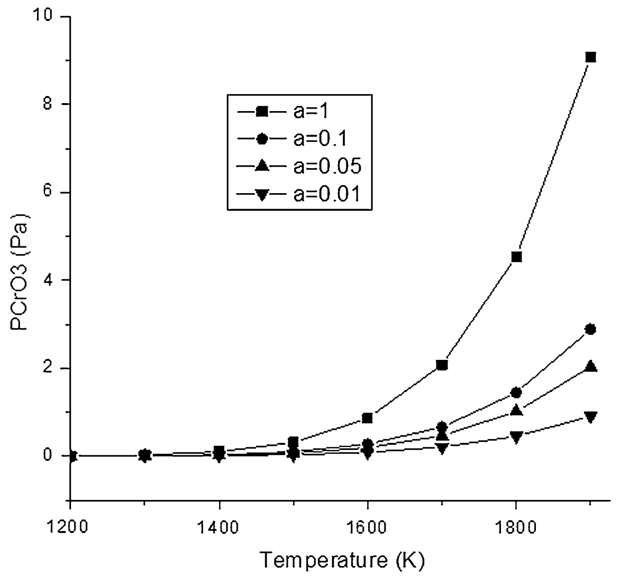

Fig. 14—The $CrO_3$(g) partial pressures (Pa) at different $Cr_2O_3$ activities as a function of temperature.

with respect to temperature. All three databases validate the decrement in entropy. Chase[23] reported the results of calorimetric measurements of the molar heat capacity, Cp, for $CrO_3$ (g) up to 6000 K (5727 °C), which form the source of JANAF data as compared by the third law analysis by the present author. This is presented in the curve presented in Figure 10.

To understand the relative stabilities of the various oxides of chromium, it would be desirable to have an Ellingham diagram that presents the Gibbs free energy of formation values ( $\Delta G_f^\circ$) as a function of temperature for these oxides. As it has been shown earlier that JANAF provides a set of consistent data, the diagram is drawn on the basis of this source alone and presented in Figure 11(a). The oxide $Cr_2O$ is not found in JANAF.

It is observed that $Cr_2O_3$ is the most stable oxide and CrO the least stable one. The lines corresponding to $CrO_2$(g) and $CrO_3$(g) cross each other around 1500 K (1227 °C). On the other hand, the difference between the $\Delta G_f^\circ$ values is extremely small. For the sake of clarity, the crossing point is magnified in Figure 11(b).

Furthermore, the standard Gibbs energy change for Reaction [8], *viz.* $\Delta G^\circ_{(8)}$

$$2\,CrO_2(g) + O_2(g) = 2\,CrO_3(g) \qquad [8]$$

is plotted in Figure 12. This line shows that oxidation Reaction [8] has a negative Gibbs energy up to 2000 K (1727 °C), indicating that the chromium emissions from oxides under oxidizing conditions are most likely to be $CrO_3$(g).

The equations for the change of the Gibbs free energy of formation $\Delta G_f^\circ$ for the various oxides corresponding to the lines in Figure 11 are presented in Table I in the form $A + BT$. The values are valid for the temperature range 400 K to 1900 K (127 °C to 1627 °C).

Seetharaman *et al.*[1] have reported that chromium oxide is emitted when chromium-containing slags are exposed to oxidizing atmosphere. The corresponding surface reaction in basic slags, where $Cr^{3+}$ is the dominating species, would be

$$2/3Cr_2O_3(\ell,\ \text{slag}) + O_2(g) = 4/3CrO_3(g). \qquad [9]$$

The changes of Gibbs energy for Reaction [8], *viz.* $\Delta G_8$, for different activities of $Cr_2O_3$ in the slag, are presented in Figure 13.

In the case of acid slags, the dominating species would be $Cr^{2+}$ as reported by Wang and Seetharaman.[3] In this case, it is surmised that the emission of $CrO_3$ might happen through the intermediate reaction stages $Cr^{2+} \rightarrow Cr^{3+} \rightarrow Cr^{6+}$. The likelihood of $Cr^{4+}$ occurring could not be verified by earlier works[16–19] and, thus, do not provide evidence for the occurrence of this species in slags even under oxidizing conditions. Figure 14 shows the partial pressures of $CrO_3$ gas at different $Cr_2O_3$ activities as a function of temperature. The $P_{CrO3}$ is increasing with increasing temperature and $a_{Cr2O3}$.

The relative stabilities of the various oxides of chromium are examined from a thermodynamic viewpoint. The inconsistencies in the existing data are presented. The Gibbs energy of $Cr_2O_3$ was calculated by third law analysis and was found to be in agreement with the data from JANAF. The literature data available for $Cr_2O_3$ are found to be reliable and are in agreement with JANAF assessment. The data for the rest of the oxides of chromium presented by JANAF show mutual consistency An Ellingham diagram for the various oxides of chromium and the equations for the $\Delta G_f^\circ$ for the formation of these oxides are presented. These results are of importance in identifying the chromium oxide species emitted when chromium slags are exposed to oxidizing atmosphere during tapping of the slag.

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