Thermochimica Acta 559 (2013) 1–16

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Review

A chemical thermodynamics review applied to V_2O_5 chlorination

E.A. Brocchi, R.C.S. Navarro*, F.J. Moura

Materials Engineering Department (PUC-Rio), Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro, Brazil

ARTICLE INFO

Article history:
Received 24 July 2012
Received in revised form 10 January 2013
Accepted 25 January 2013
Available online 6 March 2013

Keywords:
Chemical thermodynamic
V_2O_5
Chlorination

ABSTRACT

This work is mainly related to the thermodynamic study of the V_2O_5 carbon-chlorination. In this context, three different approaches of diverse complexity level were employed. First, the formation of individual vanadium chlorides and oxychlorides were considered on the basis of the well known $\Delta G^\circ \times T$ diagrams. It is suggested that these simple constructions can help in understanding the formation sequence of vanadium chlorinated species. Moreover, the relative stability of the most stable vanadium chloride (VCl_4) and oxychloride ($VOCl_3$) was addressed based on available thermodynamics data. Finally, a gas phase speciation calculation was performed in order to obtain, simultaneously, the concentration of all possible vanadium chlorides and oxychlorides as a function of temperature, Cl_2 and O_2 partial pressures. It is demonstrated that, although diverse in the complexity level, the three methods considered have a strong relation with each other, and converge to a better insight into the nature of the chemical equilibrium states achievable for the reaction system under study. The same approach can be applied to any other reaction system of technological importance.

Contents

1. Introduction

In general terms the present work can be considered as a contribution to a quantitative study review related to the chemical equilibrium of metallic oxides chlorination. Three possible ways of investigating the achievable equilibrium states will be presented. The first one is based entirely on the construction of $\Delta G^\circ \times T$ diagrams. The second one applies the reactions Gibbs energies for computing the concentration of specific chlorinated compounds of interest and enables the study of the relative stability of these species in a specific temperature range. The third and most general one is defined by the minimization of the total Gibbs energy of the system.

The three mentioned methods are then applied to the study of the thermodynamic viability of the reaction between V_2O_5 and gaseous Cl_2. The importance of the presence of a reducing agent is discussed through the construction of proper $\Delta G^\circ \times T$ in the presence as in the absence of graphite. The same method is also applied for the formulation of possible chlorination paths for the formation of the most stable chlorinated species produced at high $P(Cl_2)$ and low $P(O_2)$ values, conditions usually found in most experiments. The relative stability of the mentioned chlorides is then studied based on the independent resolution of chemical equilibrium equations. Finally, the equilibrium states available to the system are predicted through the minimization of its total Gibbs energy. The effect of T, $P(Cl_2)$ and $P(O_2)$ over the composition of the gas phase in clearly presented and discussed. Also, calculations of the enthalpy

---

* Corresponding author. Tel.: +55 2135271720.
E-mail addresses: ebrocchi@puc-rio.br (E.A. Brocchi), rogerioncs@gmail.com (R.C.S. Navarro).

0040-6031/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tca.2013.01.025

associated with the chlorination reactions are also performed, and the impact of the amount of Cl_2 available over the heat absorbed or released by the reaction system is explored. Emphasis is given to the point that the most general strategy must embrace the tendencies indicated by the implementation of simpler methodologies.

Until recently, the approach applied for chemical equilibrium studies was almost exclusively based on standard free energy versus temperature and predominance diagrams. However, nowadays, advances in computational thermodynamics have enabled a sort of software developments which can perform more complex calculations. So, it is understood that time has come for a review on thermodynamics chlorination which can combine its basic aspects with a now available new kind of approach. Therefore, the generality and depth of the produced information for this work have also motivated the authors to publish its content in a form of a chapter, which could well be considered as a part of a thermodynamic book applied to high temperature process.

1.1. *Reductive chlorination roasting*

Chlorination roasting has proven to be a very important industrial route and can be applied for different purposes. Firstly, the chlorination of some important minerals is a possible industrial process for producing and refining metals of considerable technological importance, such as titanium and zirconium. Also, the same principle is mentioned as a possible way of recovering rare earth from concentrates [1] and metals, of considerable economic value, from different industrial wastes, such as, tailings [2], spent catalysts [3], slags [4] and fly ash [5]. The chlorination processes are also presented as environmentally acceptable [6,7]. In general terms the chlorination can be described as reaction between a starting material (mineral concentrate or industrial waste) with chlorine in order to produce some volatile chlorides, which can then be separated by, for example, selective condensation. The most desired chloride is purified and then used as a precursor in the production of either the pure metal (reaction of the chloride with magnesium) or its oxide (by oxidation of the chloride).

The chlorination reaction has been studied on respect of many metal oxides [8–11] as this type of compound is the most common in the mentioned starting materials. Although some basic thermodynamic data is enclosed in these works, most of them are related to kinetics aspects of the gas–solid reactions. However, it is clear that the understanding of the equilibrium conditions, as predicted by classical thermodynamics, of a particular oxide reaction with chlorine, can give strong support for both the control and optimization of the process. In this context, the impact of industrial operational variables over the chlorination efficiency, such as the reaction temperature and the reactors atmosphere composition, can be theoretically appreciated and then quantitatively predicted. On that sense, some important works have been totally devoted to the thermodynamics of the chlorination and became classical references on the subject [12–15].

As said before, the approach applied for the study of chemical equilibrium studies was based exclusively on $\Delta G^\circ \times T$ and predominance diagrams. Nowadays, due to the development of computational thermodynamics, a more detailed calculation is possible. This approach, together with the one accomplished by simpler techniques, converge to a better understanding of the intimate nature of the equilibrium states for the reaction system of interest.

The present chapter focuses on the chemical equilibrium conditions associated with the chlorination of V_2O_5 both in the presence as in the absence of carbon (reducing agent). The impact of carbon over the thermodynamic viability of the reactions is clearly presented and discussed. Also, the equilibrium conditions are appreciated through graphical constructions of different complexity level, beginning with the well known $\Delta G^\circ \times T$ and predominance diagrams, and ending with gas phase speciation diagrams, rigorous calculated through the minimization of the total Gibbs energy of the system.

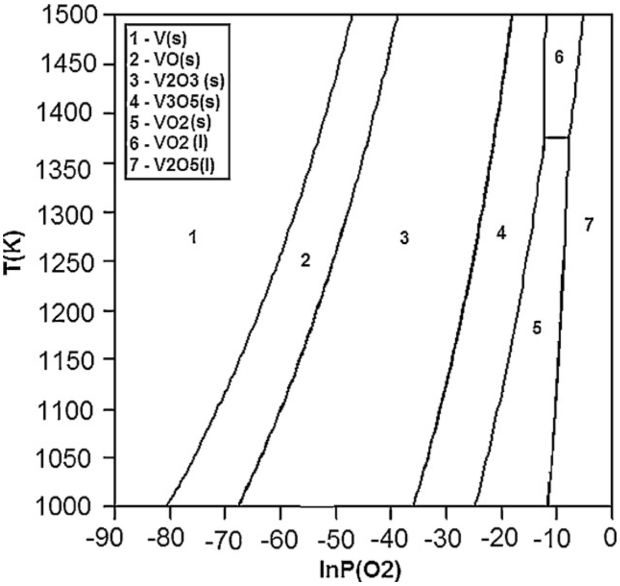

Fig. 1. Predominance diagram for the system V–O.

2. The system V–O–Cl

Vanadium is a transition metal that can form a variety of oxides. At ambient temperature and oxygen potential, the form V_2O_5 is the most stable. It is a solid stoichiometric oxide, where vanadium occupies the +5 oxidation state. By lowering the partial pressure of O_2, the valence of vanadium varies considerably, making it possible to produce a family of stoichiometric oxides: V_2O_4, V_3O_5, V_4O_7, VO, VO_2 and V_2O_3. Recently, it has been discovered that vanadium can also form a variety of non-stoichiometric oxygenated compounds [16], however, to simplify the treatment of the present review, these phases will not be included in the data-base used for the following computations. Additionally, it was considered that the concentration of the oxides in gas phase is low enough to be neglected. Further, on what touches the computations that follows, the software Thermocalc was used in all cases, and it will always be assumed that equilibrium is achieved, or in other words, kinetic effects can be neglected.

The relative stability of the possible vanadium oxides can be accessed through construction of a predominance diagram in the space T–$P(O_2)$ (see Fig. 1). As thermodynamic constraints we have $n(V)$ (number of moles of vanadium metal–it will be supposed that $n(V) = 1$), T, P and $P(O_2)$. The reaction temperature will be varied in the range between 1073 K and 1500 K and the partial pressure of O_2 in the range between 8.2×10^{-4} atm and 1 atm.

The total pressure was fixed at 1 atm. It can be seen that for the temperature range considered and a partial pressure of O_2 in the neighborhood of 1 atm, V_2O_5 is formed in the liquid state. Through lowering the oxygen potential, crystalline vanadium oxides precipitate, VO_2 being formed first, followed by V_2O_3, VO, and finally V. The horizontal line between fields “5” and “6” indicates the melting of VO_2, which according to classical thermodynamics must occur at a fixed temperature. Next it will be considered the species formed by vanadium, chlorine and oxygen.