J. Chem. Thermodynamics 43 (2011) 1224–1228

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Standard values of fugacity for sulfur which are self-consistent with the low-pressure phase diagram

Robert A. Marriott *, Herman H. Wan

Alberta Sulphur Research Ltd., University of Calgary, Alberta, Canada

ARTICLE INFO

Article history:
Received 24 October 2010
Received in revised form 24 February 2011
Accepted 10 March 2011
Available online 16 March 2011

Keywords:
Sulfur
Fusion
Phase diagram
Melting
Triple points
Vapour pressure
Allotropy
Fugacity

ABSTRACT

A method for calculating the fugacity of pure sulfur in the α-solid, β-solid and liquid phase regions has been reported for application to industrial equilibrium conditions, *e.g.*, high-pressure solubility of sulfur in sour gas. The fugacity calculations are self-consistent with the low-pressure phase diagram. As recently discussed by Ferreira and Lobo [1], empirical fitting of the experimental data does not yield consistent behaviour for the low-pressure phase diagram of elemental sulfur. In particular, there is a discrepancy between the vapour pressure of β-solid (monoclinic) and liquid sulfur at the fusion temperature. We have provided an alternative semi-empirical approach which allows one to calculate values of the fugacity at conditions removed from the conditions of the pure sulfur phase transitions. For our approach, we have forced the liquid vapour pressure to equal the β-solid vapour pressure at the β-l-g triple point corresponding to the 'natural' fusion temperature for β-solid. Many studies show a higher 'observed' fusion temperature for elemental sulfur. The non-reversible conditions for 'observed' fusion conditions for elemental sulfur result from a kinetically hindered melt which causes some thermodynamic measurements to be related to a metastable S_8 liquid. We have measured the 'natural' fusion temperature, $T^{\beta}_{fus}(\mathrm{exp.}) = (388.5 \pm 0.2)$ K at $p = 89.9$ kPa, which is consistent with literature fusion data at higher-pressures. Using our semi-empirical approach, we have used or found the following conditions for the low-pressure sulfur phase diagram: $T^{\alpha\text{-}\beta\text{-g}} = 368.39$ K, $p^{\alpha\text{-}\beta\text{-g}} = 0.4868$ Pa, $T^{\beta\text{-l-g}} = 388.326$ K, $p^{\beta\text{-l-g}} = 2.4437$ Pa, $T^{\beta\text{-l}}_{fus}(101.325\ \mathrm{kPa}) = 388.348$ K, $T^{\alpha\text{-}\beta\text{-l}} = 419.06$ K, and $p^{\alpha\text{-}\beta\text{-l}} = 124{,}360$ kPa.

1. Introduction

Ferreira and Lobo [1] recently have published a significant study which has long been needed in the literature outlining the low-pressure phase diagram of sulfur. Our group also has investigated the phase diagram of pure elemental sulfur with slightly different objectives beyond the phase transition conditions. These applications have included the use of the standard sulfur fugacity when (1) modelling sour gas and elemental sulfur equilibria for defining the sulfur carrying capacity of sour gases and (2) looking at the isochoric pressure increase associated with melting sulfur within liquid sulfur pipelines (or sometimes sulfur which has solidified in our lab equipment and is threatening to burst the equipment upon re-melting). Sulfur depositing from a sour gas can be solid or liquid; therefore, applied equilibrium models need to be self-consistent with the pure sulfur phase diagram for the prediction of equilibria between α-sulfur (orthorhombic), β-sulfur (monoclinic), liquid sulfur, and gaseous sulfur. Furthermore, the thermodynamic potentials defining the sulfur standard state must be continuous at all phase transition conditions. This is difficult to achieve through purely empirical correlations because the literature calibration data is not completely consistent.

For clarity, a schematic for the pure sulfur phase diagram is shown in figure 1. This figure has been adopted from Ferreira and Lobo [1] who show a similar phase diagram; however, we have used a slightly different labelling system. For example, our three low-pressure triple point conditions are labelled using α-β-g, β-l-g, and α-β-l *versus* Ferreira and Lobo's [1] choice to use T_1, T_2, and T_3. Using our labelling system, the triple point temperatures are $T^{\alpha\text{-}\beta\text{-g}}$, $T^{\beta\text{-l-g}}$, and $T^{\alpha\text{-}\beta\text{-l}}$ and the pressures are $p^{\alpha\text{-}\beta\text{-g}}$, $p^{\beta\text{-l-g}}$, and $p^{\alpha\text{-}\beta\text{-l}}$, respectively.

For an example of a property discontinuity, the measured vapour pressures of the β-solid sulfur [2] and liquid sulfur [3] do not intersect at the $T^{\alpha\text{-}\beta\text{-l}}$ melting point, which are required to for a continuous fugacity. This disconnect is due to the sulfur fluids being allotropic in nature and slow to achieve equilibrium, thus causing some experimental measurements to exhibit a lower than expected accuracy. In part, Ferreira and Lobo [11] discussed the issue when they attempted to use empirical fits for the phase changes to define the α-β-g triple point conditions. By definition, the vapour pressure for β-solid and liquid sulfur must be equal at the β-l-g triple point and this does not occur with simple empirical correlations. This small discontinuity can cause models based on

---

* Corresponding author. Tel.: +1 403 220 3144.
E-mail address: rob.marriott@ucalgary.ca (R.A. Marriott).

0021-9614/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2011.03.008

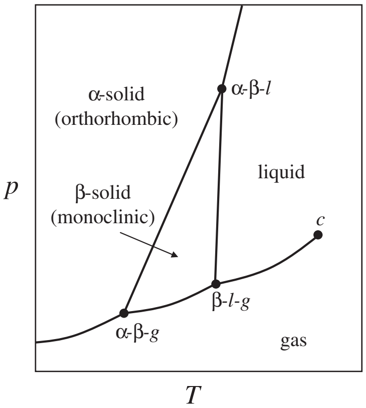

FIGURE 1. A schematic of the low-pressure elemental sulfur phase diagram. The α-β-g represents the orthorhombic–monoclinic–gas triple point, α-β-l is the orthorhombic–monoclinic–liquid triple point and β-l-g is the monoclinic–liquid–gas triple point. There were labelled T_1, T_2, and T_3, respectively, in Ferreira and Lobo's previous study [1].

the vapour pressure to be in large error at moderately higher pressures. Ferreira and Lobo's [11] approach was to specify the α-β-g and α-β-l triple point conditions based on empirical correlations and, using experimental data, integrate the Clapeyron equation for each phase transition to arrive at the β-l-g triple point. Even with that approach the vapour pressures for the β-solid and liquid do not equal one another; however, their equations match the experimentally determined phase transition lines. Our approach was to use the lower-pressure α-β-g and β-l-g triple points (with a matching vapour pressure) as reference conditions. Furthermore, we have used the so-called 'natural' fusion condition and β-l-g triple point.

Both approaches require the fusion temperatures for β-solid, T^{β}_{fus}, to determine the α-β-l triple point. Again, our group has been using a slightly different approach to calculate the low-pressure sulfur phase diagram from that of Ferreira and Lobo [11], because (1) we require the values of the liquid and solid standard fugacity at conditions far from the pure phase transitions and (2) we have used a lower β-l-g triple point temperature which corresponds to the lower thermodynamic fusion temperature. Low thermal conductivity for solid sulfur and kinetically hindered allotropic behaviour for liquid sulfur makes fusion measurements challenging and causes a difference between the 'observed' and 'natural' fusion temperature. The lower temperature fusion condition was termed the "natural" melting point by Gernez [4] who measured $T^{\beta}_{fus} = 387.8$ K. Note that in a 1976 review of elemental sulfur, Meyer [5] suggested that the $T^{\beta}_{fus} = 392.8$ K was the 'natural' melting point; whereas, an 'ideal' melting point was located at a higher temperature. If Meyer's terms are used then there is no difference between the 'observed' and 'natural' fusion temperature; therefore, for clarity we have used 'observed' to mean the higher temperature where many melts have been measured.

Our modelling efforts reported here have forced the vapour pressures to be equal at the β-l-g triple point. We report a measured 'natural' melting point and describe an alternate low-pressure elemental sulfur phase diagram which uses the lower temperature 'natural' fusion conditions for the thermodynamic melting point and β-l-g triple point. Note that this discussion does not dispute the existence of an 'observed' triple point near $T = 393.57$ K as calculated by Ferreira and Lobo [11], and many others. Where possible we have updated our approach by incorporating the equations used by Ferreira and Lobo [11], who have provided a detailed review of available experimental data. For example, Ferreira and Lobo's [11] vapour pressure for α-solid and the lower temperature α-β-g triple point has been used for consistency.

2. The semi-empirical approach

2.1. Fugacity of α-sulfur (orthorhombic)

For pure sulfur at low temperature, the small value of the vapour pressure of phase *i*, $p^{i,vp}$, leads us to assume that the vapour behaves similar to an ideal gas. The fugacity of α-sulfur, f^{α}, at higher pressure can be calculated as

$$f^{\alpha}/\text{Pa} = p^{\alpha,vp}\exp\left[\int_{p^{\alpha,vp}}^{p}\frac{V^{\alpha}_{m}}{RT}\,dp\right], \tag{1}$$

where the pressures are in Pa and V^{α}_{m} is the molar volume of α-sulfur in $\text{m}^3\cdot\text{mol}^{-1}$. The vapour pressure for α-sulfur has been calculated using the Clapeyron equation, equation (11), of Ferreira and Lobo [1]. Note that the vapour pressure equation of Shuai and Meison [6] does not yield consistent results with the accepted transition temperatures and enthalpy changes.

Given a small isothermal compressibility for the dense phase S_8, equation (1) was simplified by assuming that V^{α}_{m} is constant for a low range of pressure:

$$f^{\alpha}/\text{Pa} = p^{\alpha,vp}\exp\left[V^{\alpha}_{m}(p/\text{Pa} - p^{\alpha,vp}/\text{Pa})/R(T/\text{K})\right]. \tag{2}$$

The molar volume of α-sulfur has been calculated using a linear relationship with temperature,

$$V^{\alpha}_{m}/(\text{cm}^3\cdot\text{mol}^{-1}) = a + b\cdot T/\text{K}. \tag{3}$$

We have used two approaches for calculating the molar volume: (i) calibration of equation (3) from the dilatometric density data of Basin and Nenashev [7] for polycrystalline α-solid and (ii) optimisation of equation (3) to minimise the squared temperature difference from the high-pressure fusion measurements of Tammann [8] and Woll [9] (effective volume). For the first method, $a = 107.429$ and $b = 0.0570$ and for the optimised method $a = 125.793$ and $b = 0.0222$. Note that the optimisation in the second method required the relationship between the β-solid and liquid, discussed in sections 2.2 and 2.3.

For monocrystalline sulfur, equation (3) could have been calibrated with crystallographic data which are available below ambient conditions [10,11]. However, to utilise the crystallographic data for the solid-solid phase transition and fusion conditions, volumes must be extrapolated to temperatures greater than first triple point temperature, $T > 368.39$ K. While crystallographic volumes are in agreement at ambient conditions, there are discrepancies between the lower temperature volumes and thermal expansions, causing the extrapolations to be very different. Extrapolation from the single crystal data of Coppens *et al.* [10] leads to $V^{\alpha}_{m368.39\text{K}} = 125.0\ \text{cm}^3\cdot\text{mol}^{-1}$ and extrapolation using equation (4) of Wallis *et al.* [11] leads to $V^{\alpha}_{m368.39\text{K}} = 126.8\ \text{cm}^3\cdot\text{mol}^{-1}$. The dilatometric density data of Basin and Nenashev [7] show that polycrystalline sulfur molar volume is larger than monocrystalline volume at $T = 368.39$ K by as much as $\Delta_{mc\rightarrow pc}V^{\alpha}_{m} = 1.8\ \text{cm}^3\cdot\text{mol}^{-1}$. Bulk sulfur is polycrystalline; therefore, for the high-pressure fusion, Basin and Nenashev's [7] data are a reasonable choice. For the first approach, the dilatometric density data of Basin and Nenashev [7] show a volume of $V^{\alpha}_{m368.39\text{K}} = 128.427\ \text{cm}^3\cdot\text{mol}^{-1}$. When the α-solid volumes are optimised using the high-pressure fusion data, $V^{\alpha}_{m368.39\text{K}} = 133.971\ \text{cm}^3\cdot\text{mol}^{-1}$, which is substantially larger than that of the previous extrapolations. This larger effective volume may be due to crystallite size effects, lattice softening from increased disorder, errors in the fusion enthalpy data (short measurement time) or error associated in our vapour pressure extrapolation for the liquid. A third method was briefly explored