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Thermodynamic re-assessment of pure chromium using modified segmented regression model

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ABSTRACT

Chromium is considered an essential addition element in multiple industrial applications. Therefore, obtaining an accurate and robust description of its properties is important. Recently, several attempts were made to improve the thermodynamic description of pure elements and binary systems in the frame of the third generation CALPHAD databases. Moreover, it became increasingly important to develop mathematical tools that can allow researchers more access to each phase of the material over the entire temperature range. Thus, the recently proposed segmented regression model was modified using the so-called sigmoid function for the case of pure Cr. A comprehensive analysis of phase equilibria and thermodynamic properties of pure Cr was used to develop an updated unary description from 0 K to 6000 K using the proposed modified segmented regression (MSR) model. In addition, two newly developed machine learning tools were utilized to analyze the datasets used in this assessment to determine any possible outliers.

1. Introduction

Chromium is an important element that is well known for its unique magnetic properties and high corrosion resistance. It is most commonly used in stainless steel and chrome plating industries [1]. These industries rely heavily on the application of computational thermodynamics for the calculation of phase diagrams, which are considered as one of the main tools in alloy design, development and processing [2]. The CALPHAD (CALculation of PHAse Diagram) method is used to produce phase diagrams using modeled Gibbs energies as functions of temperature, composition and pressure. It is important to have a accurate unary descriptions as they are the basis for extrapolating binary, ternary and other higher order systems [3,4].

Several attempts were made to improve the temperature dependence of the Gibbs energy G(T) of stable solid phases and replace the SGTE (Scientific Group Thermodata Europe) polynomial description with alternative physically-based models. This was first proposed in the Ringberg workshop in 1995 [5], and these models came to be known later as the third generation CALPHAD models [6-9]. The main goal for developing third generation CALPHAD databases is to obtain a physically-based formulations for the Gibbs energies of pure elements with fitting parameters that can be associated with physical quantities, which in return can be later validated using available experimental and DFT data [6.8-11]. These alternative models became even more necessary in recent years as the need for an accurate description at low temperatures became essential for many engineering applications [12]. However, one of the main applications of Cr is using it as an additive in multicomponent alloy design applications. Therefore, it is equally important to improve its thermodynamic description above the melting point as well. In this approach, this is achieved by using the so called sigmoid function to obtain a smooth description that expands above the melting point and covers the whole temperature range.

In this paper, a review of the available thermodynamic and phase equilibria data of pure Cr will be provided, along with a review of the previous modeling strategies used for pure Cr. After selecting the most accurate model using statistical goodness of fit criteria, a modification using the sigmoid function will be introduced in order to improve the unary system descriptions and expand the approach beyond the melting point, so it would also be able to include different available model descriptions for different temperature zones and connect between them [13]. In addition, the datasets will be validated using the outlier detection method [13] and the cross validation method [14].

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Table 1

Experimental data sets for heat capacity at constant pressure (Cp) of pure Cr.

Notation in Figures	Reference	Year	Temperature range, K	Reported error, %	Composition (weight percent)	Measurement method
37AND	[16]	1937	56–291	< 1	99.35 Cr, 0.65 O_2 and N_2	
52EST	[17]	1952	1.82-3.99	< 1	99.9 Cr	vacuum calorimeter
79KEM	[18]	1979	263–344	< 2		differential scanning calorimeter
60BEA	[19]	1960	267-323	< 1	99.8 Cr	adiabatic calorimeter
65KOH	[20]	1965	320-1800	< 2		adiabatic calorimeter
50ARM	[21]	1950	273–1073	< 1		adiabatic calorimeter
65KAL	[22]	1965	60–300	< 0.5		
58KRA	[23]	1958	964–1598	2–5	99.8 Cr	adiabatic calorimeter
58MAR	[24]	1958	823-1223	< 1		adiabatic calorimeter
27SIM	[25]	1927	71.29–78.52	< 1	99.9 Cr	vacuum calorimeter
62CLU	[26]	1962	14.1-274.4	< 0.7	99.9 Cr	
56RAY	[27]	1956	1.78-4	< 1	99.8 Cr	mechanical heat switch calorimeter
34JAE	[28]	1934	672.8–2150	< 0.3		
88LIN	[15]	1988	300-2131	2–5	99.5 Cr	levitation calorimeter
81TOU	[29]	1981	25–2123	< 1		



Figure 1. Heat capacity datasets for pure Cr.



Fig. 2. Heat capacity datasets for pure Cr with discrepancies shown.

2. Literature review

A review of experimental data, phase transformation and thermodynamic properties for pure Cr available in literature is summarized in the following sections.



Fig. 3. Heat capacity datasets for pure Cr for low temperature region (\leq 300) with discrepancies shown.

Table 2
Experimental data sets for relative enthalpy (H) for pure Cr

 I · · · ·			1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1	I i i i i	
Notation in Figures	Reference	Year	Temperature range, K	Reported error, %	Composition (weight percent)
10Sch	[30]	1910	83–373	< 2	98.97 Cr
14Sch	[31]	1914	374–867	< 2	98.95 Cr
26Umi	[32]	1926	373–1913		
56Luc	[33]	1956	303-1883	< 10	
65Con	[34]	1965	1260-2092	< 1	99.99 Cr
88Lin	[15]	1988	1641-2020	< 3	99.5 Cr

2.1. Review of heat capacity data

Experimental heat capacity datasets were collected from different sources. These data sets are summarized in Table 1 and can be seen in Fig. 1. In addition, one dataset [88LIN] was used by Thurany [9] in his model of pure Cr. This dataset, provided by Lin and Frohberg [15], was obtained by fitting measured enthalpy data using the least squares method and deriving the heat capacity data function of temperature. For that reason, this dataset was excluded from this assessment. In addition, Figs. 2 and 3 show the discrepancies in the data based on the errors reported with each experimental dataset.



Fig. 4. Enthalpy datasets for pure Cr.

Table 3

Recommended enthalpy of fusion for pure Cr from different sources.

Enthalpy of fusion, <i>KJ</i> / mol	Accepted melting point, <i>K</i>	Reference	Year	Comments
$\begin{array}{c} 15.3\\ 29.6\pm0.5\end{array}$	2130	[35]	2002	Commercial source,
	2136	[15]	1988	99.5% Cr
16.9	2180	[36]	1973	
21	2180	[37]	1991	

Table 4

Recommended melting points for pure Cr from different studies.

Melting point (K)	Reference	Year	Comments
2133 ± 20	[46]	1949	Extrap. to zero N, O content
2118 ± 10	[47]	1951	Thermal analysis, induction heating, extrap. to zero N, O content
2176 ± 10	[48]	1952	High purity samples
2122 ± 20	[49]	1959	
2133 ± 6	[42]	1967	
2133	[36]	1973	
2180	[40]	1982	
2133 ± 50	[50]	1990	Estimated from binary Cr-O phase diagram
2136 ± 50	[51]	1994	Estimated from binary Cr-O phase diagram
2133	[9]	1998	
2115 ± 20	[52]	2001	Pulsed heated technique from NIST
2136	[38]	2010	

2.2. Review of relative enthalpy and enthalpy of fusion data

The experimental data collected from different sources were used in the present assessment to validate the results obtained by comparing with the calculated relative enthalpy curve. A summary of the relative enthalpy data sets used in the present assessment is available in Table 2 and a plot of the data can be seen in Fig. 4. A list of the different enthalpy of fusion values from different studies can be found in Table 3.

2.3. Phase equilibria

In their investigation of the Fe–Cr system, Xiong et al. [38] reported a large discrepancy between the experimental data and their assessments of phase equilibria concerning the liquidus and solidus. They also mentioned the high melting point value of pure Cr in the SGTE unary database [37], 2180 K, as the main reason. That value was based on the assessment of Anderson [39], who adopted the value chosen by Gurvich

et al. [40]. It was later reported by Rudy and Windisch [41], who used the Pirani method [42], that the melting point value is 2133 ± 6 K. This finding was not considered in the compilation done by Gurvich et al. [38]. On the other hand, the results obtained using the Pirani method [43] and other pyrometer based methods can have significant uncertainties at high temperatures, where it becomes very difficult to observe the formation of liquid. Nonetheless, a compilation published by Hultgren et al. [36] adopted the melting point, 2133 K, after previously accepting the value of 2176 K almost ten years earlier [44]. In addition, ASM International's phase diagram compilation recommends the melting point value of 2136 K for pure Cr [45]. On the other hand, it is also worth mentioning that it is common practice to use the melting point values of pure elements to calibrate the system before performing any experiments. This may be the reason why such a large discrepancy was observed by Xiong et al. [38] as it is a common problem with all Cr containing systems. Moreover, having gas impurities in the system can play a role in decreasing the melting point of Cr. At the end, it was decided in this work to consider the melting point for pure Cr to be 2136 K, in accordance with the recommendation of Xiong et al. [38]. A brief summary of the recommended melting points from different studies for pure Cr can be found in Table 4.

2.4. Magnetism

The magnetic properties of Cr is a topic that many theoretical and experimental studies focused on resolving [53,54]. There is a general agreement that Cr is antiferromagnetic at low temperatures [9,54], and that the Néel temperature is approximately 311 K [9,44,54,55]. On the other hand, there is a debate regarding Cr magnetic properties at high temperatures [38,54]. A number of different studies indicated a strong magnetic contributions in Cr at high temperatures [56,57]. On the other hand, other studies mention that the magnetic contribution above the Néel temperature is negligible [9,19,38,39,55]. The magnetic contribution for Cr was ignored in this assessment in accordance with the assessment done by Xiong et al. [38].

3. Thermodynamic model from 0 K until the melting point

3.1. Modeling strategies

In this section, a brief summary of the main thermodynamic models used for previous assessments of pure Cr will be discussed. Then a statistical comparison between the main models will be performed in order to choose the most accurate model to describe pure Cr from 0 K to the melting point.

3.1.1. Andersson and SGTE models

In 1985, Andersson [39] utilized a polynomial expression for Gibbs energy as a function of temperature based on the available thermodynamic data. The results were then validated by comparing the calculated heat capacity with available experimental data. It is worth mentioning that the Gibbs energy description did not cover the temperature range below the room temperature. This approach was similar to the SGTE approach that was proposed later in 1991 by Dinsdale et al. [37], where the Gibbs energy was represented using a power series in terms of temperature. Despite the widespread use, this approach has four main disadvantages. The first one is the use of high-order polynomials, which can cause an over-fitting problems that may lead to unstable models. Another issue is that, similar to the approach by Andersson, the SGTE description covers temperatures higher than 298.15 K and does not cover low temperature ranges. In addition, the SGTE parameters were chosen as a matter of convenience and not necessarily with physical considerations in mind [3]. Finally, the use of a discontinuity at the melting point in the heat capacity curve have caused some stoichiometric phases in the SGSOL (SGTE solution database) to have some serious abnormalities, resembling a second phase transition, which has frustrated attempts to include them in the SGTE substance database (SGSUB) [58].

3.1.2. Thurnay model

In 1998, Thurnay proposed a mathematical model to describe thermophysical properties of transition metals [9]. He attempted to use the Debye function to describe the heat capacities accurately in the low temperatures range. It also used Debye-like functions to calculate the linear thermal expansion coefficients, which ensured a correct behaviour of the thermal expansion function at temperatures below the Debye temperature [9]. The heat capacity was described as a summation of three terms

$$C_p^{TH}(T;\boldsymbol{\theta}^{TH}) = C_p^{Deb}(T;\boldsymbol{\theta}_D) + C_p^{Hoch}(T;b,d) + C_p^{Exp}(T;g,h),$$
(1)

where *T* is the temperature in Kelvin and $\theta^{TH} = (\theta_D, b, d, g, h)$ is the vector of unknown model parameters to be estimated from available data. Here, the first term $C_p^{Deb}(T)$ was introduced to describe the contributions of the free electrons and the vibration of the crystal-lattice [9, 59] by the Debye model (2), which remains constant above the Debye temperature and has the form

$$C_P^{Deb}(T;\theta_D) = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx,$$
(2)

where θ_D is the Debye temperature in Kelvin and *R* is the universal gas constant in $J/(mol \cdot K)$. The second term $C_p^{Hoch}(T)$ was proposed by Hoch to consider the electronic and vibrational contributions [59].

$$C_P^{Hoch}(T;b,d) = b T + d T^3,$$
(3)

and the last term C_{P}^{Exp} was introduced to describe the increase in the temperature for some transition metals due to the their magnetic state or crystal structure change using an exponential function

$$C_P^{Exp}(T;g,h) = e^{g+Th}.$$
(4)

3.1.3. Vřešťál-Pavlů model

Another approach was proposed in 2012 by Vřešťál et al. [60] to extend the current SGTE polynomial description down to 0 K using a slightly modified formulation of the model derived by Chen and Sundman (6) in 2001 [6]. The modified Chen-Sundman (MCS) model is expressed as a combination of the Einstein function and several polynomial terms (6). The MCS model was used in Refs. [60] to obtain the temperature dependence of the heat capacity from 0K up to the limiting temperature T_{lim} , which is usually 298.15 K, but can be slightly different in some cases. After T_{lim} the model proposed by *Vřešťal* at al. in 2012 [60] with improved coefficients values obtained by Pavlå et al. [61] in 2015 relies the current SGTE description. The general formulation of *Vřešťal*-Pavlå (VP) model to describe the temperature dependency in the heat capacity from 0K has the form

$$C_p^{VP}(T) = \begin{cases} C_p^{MCS}(T), & 0 \le T \le T_{lim} \\ \\ C_p^{SGTE}(T), & T_{lim} \le T, \end{cases}$$
(5)

where the MCS model is defined as

$$C_p^{MCS}(T;\boldsymbol{\theta}^{MSC}) = C_p^{Ein}(T;\boldsymbol{\theta}_E) + aT + bT^4 + cT^2.$$
(6)

with the vector of unknown model parameters $\theta^{MCS} = (\theta_E, a, d, c)$ to be estimated. Here, the first term is the Einstein model

$$C_{P}^{Ein}(T) = 3R \left(\frac{\theta_{E}}{T}\right)^{2} \frac{e^{\theta_{E}/T}}{\left(e^{\theta_{E}/T} - 1\right)^{2}},$$
(7)

where parameter θ_E is the Einstein temperature in Kelvin. The second

term *aT* in MCS model is related to electronic excitation and low order anharmonic corrections, and the third term bT^4 corresponds to the highorder anharmonic corrections [10]. The last term cT^2 was added by Vřešťal et al. to the original Chen-Sundman model to ensure a smooth transition between the heat capacity at low temperature using MCS (6) and the current SGTE description at T_{lim} [60,61]. This was achieved by solving a system of equations to define the unknown model parameters of the MCS model (6) and to produce a description that can imitate the behaviour of the heat capacity curve for low temperatures to some extent. A smooth connection between the heat capacities and Gibbs energy descriptions for low temperatures down to 0 K and the current SGTE Gibbs functions was ensured by equality conditions on their values and the values of their first derivatives at the T_{lim} . This means that the model parameters were not fitted with any experimental data in the original formulation of VP model [60]. In 2015, Pavl \dot{u} et al. provided an updated version of the model parameters, where the Einstein temperatures $\theta_{\rm F}$ were obtained by fitting experimental heat capacity data, and, for some elements, by using ab initio calculations [61].

3.2. Segmented regression model

A novel physically-based approach was proposed by Roslyakova et al., in 2016 that was based on the segmented regression (SR) approach [10]. The SR model (8) consists of three terms

$$C_P^{SR}(T;\boldsymbol{\theta}^{SR}) = C_P^{Deb}(T,\theta_D) + C_P^{bcm}(T,\beta_1,\beta_2,\tau,\gamma) + C_P^{magn}(T),$$
(8)

where $\theta^{SR} = (\theta_D, \beta_1, \beta_2, \tau, \gamma)$ is the vector of unknown parameters to be estimated. The first term is the Debye model (2). The second term uses the bent-cable model to decompose the physical functions at low and high temperatures which are described using linear functions

$$C_P^{bcm}(T;\beta_1,\beta_2,\tau,\gamma) = \beta_1 T + \beta_2 \cdot q(T;\tau,\gamma)$$
(9)

with the term q defined by $q(T; \tau, \gamma) = \frac{(T-\tau+\gamma)^2}{4\gamma} \mathbf{1}\{|T - \tau| \le \gamma\} + (T - \tau)\mathbf{1}\{T > \tau + \gamma\}$, where $\mathbf{1}\{\cdot\}$ is an indicator function, e.g. $\mathbf{1}\{T > \tau + \gamma\} = 1$ if $T > \tau + \gamma$ and 0 otherwise. The third term C_p^{magn} is the magnetic contribution of the heat capacity described by the Inden-Hillert-Jarl model [62]. A more accurate approximation was proposed by Chen and Sundman [6] in 2001, and further improvements were reported by Xiong et al. [63].

This approach provided an alternative thermodynamic modeling strategy that made it possible to consider the different physical contributions of the heat capacity at low and high temperatures. The SR model has been applied successfully to 18 pure elements, 5 compounds and several binary systems [10,64–66].

3.2.1. Statistical approach for model comparison

The comparison of existing models that were proposed earlier has been performed in this work using a more statistically consistent approach as an alternative to the usual strategy of relying on the researcher's subjective opinion to choose the most appropriate model (MAM) that would best describe the data. This would provide researchers with a quantitative statistical tool that has the predictive properties to assist with choosing an appropriate model for the data collected or generated. The data can be modeled using a nonlinear regression model of the form

$$y_i = C_P(T_i, \boldsymbol{\theta}) + \varepsilon_i, \quad i = 1, \dots, n,$$
(10)

where $\theta \in \mathbb{R}^p$ is a vector of unknown parameters, n is the number of observations and y_i and $C_P(T_i, \theta)$ are experimental and estimated values of the heat capacity at the temperature T_i , i = 1, ..., n. It is assumed that ε_i are independent random variables that are normally distributed with a mean 0 and a variance σ^2 .

Usually, the least square method is used to estimate the parameters,



Fig. 5. Fitted heat capacity using TH, VP and SR models compared with the experimental data for pure Cr.



Fig. 6. Fitted heat capacity using TH, VP and SR models from 0K until T_{melt} for pure Cr.

Table 5 Goodness of fit criteria (RSE, AIC, BIC) for the TH, VP and SR models for pure Cr.

Statistics	SR	TH	VP	MAM
RSE	0.8749	29.65	0.9909	SR
AIC	1237.3	48089.61	1633.632	SR
BIC	1258.159	48128.71	1646.234	SR

say $\hat{\theta}_n$, of a given model by minimizing the residual sum of squares over parameter space Θ

$$\widehat{\boldsymbol{\theta}}_n = \arg\min_{\boldsymbol{\theta} \in \Theta} \sum_{i=1}^n \left(y_i - C_P(T_i, \boldsymbol{\theta}) \right)^2.$$
(11)

The statistical goodness-of-fit criteria can then be calculated for each model. One criterion that is commonly used to compare different models is the residual standard error (RSE), which measures the difference between the data provided and the fitted regression curve, defined as

$$RSE^{j} = \sqrt{\frac{\sum_{i=1}^{n} \left(y_{i} - C_{P}^{j}(T_{i}, \widehat{\theta}_{n}^{j})\right)^{2}}{n - p^{j} - 1}}.$$
(12)

Here $G_P^i(T_i, \widehat{\theta}_n^i)$ is the estimated heat capacity at temperature T_i with j^{th} model and p^j is the number of the parameters and $\widehat{\theta}_n^j$ is the vector of the estimated parameters in the j^{th} model.

Other goodness-of-fit criteria are the Akaike's information criteria (AIC) and the Bayesian information criteria (BIC), defined as

$$AIC^{j} = n \ln \sum_{i=1}^{n} \left(y_{i} - C_{P}^{j} \left(T_{i}, \widehat{\boldsymbol{\theta}}_{n}^{j} \right) \right)^{2} + p^{j},$$
(13)

$$BIC^{j} = n \ln \sum_{i=1}^{n} \left(y_{i} - C_{p}^{j} \left(T_{i}, \widehat{\boldsymbol{\theta}}_{n}^{j} \right) \right)^{2} + p^{j} \ln n.$$
(14)

The AIC and BIC criteria have the advantage of accounting for the model complexity (the number of parameters p^j here) as a penalty term in comparison to the RSE value. This can prevent the overfitting effect from occurring as one would try to find a model that would minimize both the RSE and the number of parameters [10,67]. For all the mentioned criteria, the smallest value of statistic refers to the appropriate model.

3.2.2. Validation of existing models

The results obtained by the TH (1), VP (5) and the SR (8) models were compared with the experimental data sets listed in Table 1. The fitting results can be seen for temperatures below 300 K and 120 K in Fig. 5a and b respectively. The results from 0K until the melting point are presented in Fig. 6. It is clear that the TH model was affected by the dataset [88LIN] which causes a diversion from the results obtained by the SR and PV descriptions. As for the model comparison, statistical goodness of fit criteria (12, 13, 14) were used to compare the three models and the results are listed in Table 5.

It is clear from the results shown in Figs. 5 and 6 and Table 5 that the SR model provides the best fit from 0 K until the melting point. Despite that, the SR model still depends on the SGTE description above the melting point, and with the increasing amount of available DFT and experimental data it is even more necessary to make the SR model more flexible and completely independent from the SGTE polynomial



Fig. 7. Simple sigmoid function.

description.

4. Expansion of model beyond melting point

In this work, a mathematical tool was implemented to expand the SR approach after the melting point, so it would also be able to include different available descriptions for different temperature zones and connect between them. This was possible by employing a special logistic function that has a characteristic shape (S) curve, known as the sigmoid function. For the case of pure Cr, this modification will make it possible to adapt a new melting point, 2136 K, and would also result in a smooth transition at the melting point contrary to the SGTE description which introduces an artificial break point at the melting temperature [37].

It is also important to keep in mind that nonphysical heat capacity behaviours can results in an artificial appearance of a phase above its stability temperature range. For that reason, choosing to model the heat capacity of the solid phases as a constant above the melting point should provide sufficient negative driving force to suppress the reappearance of that phase at high temperatures [4].

Heat capacity behaviour are usually assumed to be a constant value after the melting point in the case of high melting metals (with $T_m >$ 900 K) [68]. This is because it is rather difficult to obtain reliable Cp data in that region. As for low melting point metals, it was found by Grimvall [69] that there is a gradual transition in C_V values from the well known

the point where the superheated solid phase became highly unstable, the description was then stabilized at the same value of C_p^l and not forced back to the heat capacity value of the liquid phase. This was done to avoid identifying the solid phase as stable in a region where it is supposed to be metastable [70].

For this work, the main purpose was to develop a simple, yet effective, tool for expanding the temperature range of stable solid phases that can be adjusted easily to adapt the different behaviours of the heat capacity mentioned in the previous studies.

4.1. Sigmoid function

During the process of expanding the SR model, it was necessary to include a mathematical function that can join between the different descriptions in different temperature zones without adding many new parameters that would further complicate the model. The sigmoid function was chosen to be incorporated into the SR model. The sigmoid function is a special logistic function that has a characteristic (*S*) shape curve. It is defined as a differentiable function that is real, and has real input values and a derivative that is positive everywhere. It usually provides a suitable smooth connection between nonlinear functions [71]. It is commonly used because it is nonlinear and its derivative is considered computationally simple [71]. The equation of a regular logistic function is written as

$$f(x,c_1,c_2,c_3) = \left(\frac{c_1}{1 + \exp(-c_2(x - x_0))}\right) - c_3,$$
(15)

where c_1 is the parameter for the dynamic range of the function, c_2 is the parameter for the slope of the function, c_3 is the parameter for the symmetry (or bias) of the function, and x_0 is the transition point. Fig. 7 shows the behaviour of the simple sigmoid function where $c_1 = 1$, $c_2 = 1$, $c_3 = 0$ and $x_0 = 0$. The rest of this section will discuss the applications of different sigmoid functional forms used in the MSR model.

4.1.1. Algebraic sigmoid function

By using an algebraic form of the sigmoid function (17), it was possible to obtain the expression of Gibbs energy for the solid and liquid phases for Pure Cr as can be seen in Table 6. However, using this form of the sigmoid function didn't allow for a smooth connection between the heat capacity description provided by the SR model and the heat capacity in the liquid phase C_p^l , which is equal to 50.71 *J/mol-K* for the case of pure Cr [9]. Instead, it was possible to only produce a continuous connection for this case. After applying the algebraic sigmoid function, the MSR model can be written as

$$C_P^{MSR}(T; \boldsymbol{\theta}^{MSR}) = \begin{cases} C_P^{SR}(T; \boldsymbol{\theta}^{SR}), & 0 \le T \le T_{int} \\ (1 - \sigma(T; \alpha, x_0)) C_P^{SR}(T_{melt}; \boldsymbol{\theta}^{SR}) + (\sigma(T; \alpha, x_0)) C_P^l, & T_{int} \le T \le T_{end} \end{cases}$$
(16)

Dulong – Petit 3*R* value toward the value of 2*R* after the temperature increases above the melting point. For the above mentioned reasons, it was chosen to model the solid and liquid phases as a constant value after the melting point for pure Cr.

A model proposed by Bigdeli et al. [70] attempted to provide a solution where the finite temperature DFT results were extrapolated beyond the experimental melting point T_{exp} in order to extend the description of the solid phase until the point where the superheated solid collapsed into the liquid phase. This extrapolation was then limited to the point where the solid phase became highly unstable, which was, for the case of pure Al, equal to $1.28 \cdot T_{exp}$. After the extrapolation reached

where transition weighing function $\sigma(T; \alpha, x_0)$ is defined as

$$\sigma(T; \alpha, x_0) = \frac{\frac{T - x_0}{\alpha}}{\sqrt{1 + \left(\frac{T - x_0}{\alpha}\right)^2}},$$
(17)

and $\theta^{MSR} = (\theta^{SR}; \alpha, x_0) = (\theta_D, \beta_1, \beta_2, \tau, \gamma; \alpha, x_0)$ is the vector of unknown parameters to be estimated. In addition to the SR model parameters, x_0 is the transition point and α is the slope of the connection curve after the melting point. T_{int} is the interval temperature, T_{end} is the temperature

Functions

Table 6

BCC_A2	$-13245.18 - 2.89 \times 10^{-3} T^2 + \text{GEINCR(T)}$	$0.0 \leq T \leq 531.8$
	$-13691.13 + 14.53T + 1.83 \times 10^{-3} T^2 - 1.48 \times 10^{-6} T^3 - 2.51T lnT + \text{GEINCR(T)}$	$531.8 \leq T \leq 1901.5$
	$6689.11 - 212.16T - 1.51 \times 10^{-3}T^2 + 29.63T \ln T + \text{GEINCR}(T)$	$1901.5 \leq T \leq 2136$
	$376.40T - 8.87\sqrt{T^2 - 4272T + 4.56\times10^6} - 5.66\times10^4 + 8.87T\ln - 2136 + T + \sqrt{T^2 - 4272T + 4.56\times10^6} + 10^{-10}61666666 + 10^{-10}666666666666666666666666666666666666$	$2136 \leq T \leq 6000$
	$8.87T ln(178.07 \sqrt{T^2-4272T+4.56 \times 10^6} \ -178T+380508)/T-59.58T lnT$	
Liquid	$9204.82 - 11.19T - 3.21 \times 10^{-3}T^2 + 6.90 \times 10^{-7}T^3$	$0.00 \leq T \leq 298.15$
	$13545.28 + 146.05T - 26.91T lnT + 1.89 \times 10^{-3} T^2 - 1.47 \times 10^{-6} T^3 + 139250 T^{-1} + 2.37 \times 10^{-21} T^7 + 1.000 T^{-1} + 1.000 T^{-$	$298.15 \leq T \leq 2136$
	$-1813.30 + 338.84T + 0.99\sqrt{T^2 - 4272T + 4.56 \times 10^6} - 16034.49 - 0.99T \ln - 2136 + T + \sqrt{T^2 - 4272T + 4.56 \times 10^6} - 16034.49 + 100000000000000000000000000000000000$	$2136 \leq T \leq 6000$



 $0.997 \ln(178.07\sqrt{T^2 - 4272T + 4.56 \times 10^6} - 178T + 380508)/T - 49.71T \ln T$

GEINCR(T) = $0.3490885 (24.942 \ln(\exp 251.17/T - 1)T) + 0.6497553 \times (24.942 \ln(\exp 432.55/T - 1)T)$

Fig. 8. Algebraic sigmoid function: example of heat capacity of pure Cr.



Fig. 9. Algebraic sigmoid function: range of α parameter.

limit and T_m is the melting point. The transition point x_0 and the interval temperature T_{int} were set equal to T_{melt} , and the second interval of the model was adapted to use the constant value of the heat capacity at the melting point $C_P^{SR}(T_{melt}; \theta^{SR})$ instead of the whole $C_P^{SR}(T; \theta^{SR})$ as a function. The application of this form of the MSR model can be seen in Fig. 8 for pure Cr, and the range of the α parameter can be seen in Figs. 9 and 10.



Fig. 10. Algebraic sigmoid function: range of α parameter with changing C_p^l values.



Fig. 11. Heat capacity description of pure Cr using the MSR model with the simple function.

4.1.2. Simple sigmoid function

As a suggested alternative method, the simple sigmoid function was utilized as a weighting factor $\sigma(\alpha, x_0)$ defined in (19) and implemented in the MSR model (18) in order to provide a smooth connection between the heat capacity description provided by the SR model with the constant value of the heat capacity in the liquid phase C_p^l . This can be seen in the MSR model formula

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Fig. 12. MSR model using the simple function compared with SR model for pure $\mbox{Cr}.$



Fig. 13. MSR model using the simple function compared with SR model for pure Cr.



Fig. 14. Simple sigmoid function: range of x_0 parameter.



Fig. 15. Simple sigmoid function: range of x_0 parameter with changing C_p^l values.



Fig. 16. Fitted heat capacity using MSR, TH and VP models for pure Cr over the entire temperature range.

 Table 7

 Estimated parameters values of the MSR and TH models for pure Cr.

Model	Parameter	Value	Units
MSR	θ_D	491.766	K
	$\beta_1 \cdot 10^3$	5.622	mJ
	$eta_2{\cdot}10^2$	2.222	mol·K ² mJ mol·K ³
	τ	1132.748	K
	γ	432.592	K
	α	60	
TH	$ heta_D$	500	K
	b	0.0035	J
	d	$3.0\cdot10^{-9}$	$mol \cdot K^2$ J $mol \cdot K^4$
	g	-2.1	-
	h	0.0021	1
			K

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Fig. 17. Outlier detection method heat capacity results for pure Cr.



(a) Relative enthalpy vs. temperature

(b) Difference of relative enthalpy vs. temperature

Fig. 18. Outlier detection method relative enthalpy results for pure Cr.

Table 8
Outlier detection method results for pure Cr.

Estimator - Case	All datasets	Without [34JAE]
RMSE	40831.23	40427.07
AIC	136933.2	135874.4
BIC	136966.7	136407.9

$$C_{P}^{MSR}(T; \boldsymbol{\theta}^{MSR}) = \begin{cases} C_{P}^{SR}(T; \boldsymbol{\theta}^{SR}), & 0 \le T \le T_{int} \\ (1 - \sigma(T; \alpha, x_{0})) C_{P}^{SR}(T; \boldsymbol{\theta}^{SR}) + (\sigma(T; \alpha, x_{0})) C_{P}^{l}, & T_{int} \le T \le T_{end} \end{cases}$$

where the transition weighing function $\sigma(\alpha, x_0)$ is defined as

$$\sigma(T;\alpha,x_0) = \frac{1}{1 + \exp((T_m + x_0 - T)/\alpha)},$$
(19)

with the unknown parameters vector $\boldsymbol{\theta}^{MSR} = (\boldsymbol{\theta}^{SR}; \alpha, \boldsymbol{x}_0) = (\theta_D, \beta_1, \beta_2, \tau, \gamma; \alpha, \boldsymbol{x}_0)$ to be estimated. The parameters \boldsymbol{x}_0 and α were chosen to be 47

Table 9

Comparison between parameters values before and after applying the outlier detection method.

Dataset excluded	Parameter	Value	Units
None	θ_D	491.583	К
	$\beta_1 \cdot 10^3$	5.622	mJ
	$\beta_2 \cdot 10^2$	2.222	$mol \cdot K^2$ mJ $mol \cdot K^3$
	τ	1132.748	K
	γ	432.592	K
	α	60	-
[34JAE]	θ_D	493.630	K
	$\beta_1 \cdot 10^3$	5.781	mJ
	$\beta_2 \cdot 10^2$	2.435	$mol \cdot K^2$ mJ $mol \cdot K^3$
	τ	1216.717	K
	γ	684.846	K
	α	60	-

and 17, respectively. T_{int} was set equal to 2036 K for the case of pure Cr. These values were chosen because they ensure that the maximum value of the heat capacity curve remains at the melting point, while maintaining a smooth connection between the two parts of the model separated by T_{int} . The application of the MSR model using the simple sigmoid function (19) can be seen in Fig. 11 for the case of pure Cr.

One disadvantage of using this method would be the decrease of the maximum value of the heat capacity at the melting point by 2.05%, which is equal to $1.33 J/mol \cdot K$, for pure Cr. This can be seen in Fig. 12 and in more detail in Fig. 13, where a comparison between results of the MSR and the SR models can be seen.

This function can be even more useful when trying to extrapolate the behaviour of C_p^{solid} outside the solid phase by varying the values of x_0 and C_p^l as can be seen in Figs. 14 and 15. This can be linked to the model proposed by Bigdeli et al. [70], mentioned earlier in this section.

Despite the potential applications, this form of the MSR model cannot be applied to all software as it is not mathematically possible to derive the analytic description of the Gibbs energy using the simple sigmoid function. For that reason, it was not possible to produce the TDB file. Despite that, this method have the potential to be applied in the ESPEI software where such limitations do not exist [65]. It can also be used to extrapolate the solid phase description beyond the melting point



(a) Heat capacity behaviour for solid phase of pure Cr.

while keeping the description smooth throughput the whole temperature range.

5. Implementation using ESPEI and PyCalphad

As new functional forms for the Gibbs energy for the pure elements are developed that extend the simple polynomial descriptions, it is necessary for these models to be developed within and integrated into the current state of the art CALPHAD calculation software. Currently, among the widely used existing software for CALPHAD-type calculations implementing the Compound Energy Formalism (CEF) [72–77], only pycalphad [73] supports the construction and manipulation of symbolic representations of both Gibbs energy and arbitrary property models. In

Table 10

Comparison between parameters values before and after applying the UKFCV method.

Status	Parameter	Value	Units
Before UKFCV	θ_D	491.583	К
	$\beta_1 \cdot 10^3$	5.622	mJ
	$\beta_2{\cdot}10^2$	2.222	$mol \cdot K^2$ mJ $mol \cdot K^3$
	τ	1132.748	K
	γ	432.592	К
	α	60	-
After UKFCV	θ_D	493.420	K
	$\beta_1 \cdot 10^3$	5.765	mJ
	$\beta_2 \cdot 10^2$	2.369	$mol \cdot K^2$ mJ $mol \cdot K^3$
	τ	1190.541	K
	γ	623.327	К
	α	60	-

Outlier detection method results for pure Cr.

Source	$C_P^{298},J/(\mathit{mol}\cdot K)$	$S^{298}, J/K$	θ_D^{298} , K
MSR - outlier detection result	23.573	23.702	493.630
MSR - UKFCV result	23.584	23.734	493.420
Literature	23.200 [22]	23.597 [79]	424 [80]



(b) calculated weight.



(a) Fitted heat capacity

(b) Relative enthalpy





Fig. 20. Fitted and calculated thermodynamic quantities for pure Cr using the MSR model with the algebraic function.

pycalphad, any symbolic expression supported by SymPy [78] can be used in a model, including the sigmoid function used here, with the restriction that expressions for the Gibbs energy must be differentiable.

Recently, the ESPEI software package [65], which uses pycalphad as the underlying CALPHAD calculation engine, has been used to develop a binary description for Cu–Mg that used a segmented regression model for the Gibbs energy of fcc Cu and hcp Mg [65]. ESPEI can be used to optimize and perform uncertainty quantification on the unary Gibbs energy models alone or as part of a larger assessment. Alternatively, predetermined unary models can be used in multicomponent assessments to maintain compatibility between assessments, as in the typical CALPHAD approach.

6. Outlier detection and unequal K-Fold cross-validation (UKFCV) methods

The obtained results from the MSR (blue line), TH (black line) and VP (red line) models can be seen in Fig. 16, where the parameters values for the TH model (1) were

$$\begin{aligned} \theta_D &= 500K, \\ b &= 0.0035 \ \frac{J}{mol \cdot K^2}, \\ d &= 3.0 \cdot 10^{-9} \ \frac{J}{mol \cdot K^4}, \\ g &= -2.1, \\ h &= 0.0021 \ \frac{1}{K}. \end{aligned}$$

Moreover, it is clear that the SGTE value for the melting point doesn't

agree with the majority of recent studies, as was shown in Table 4. The parameters values used for the MSR and TH models are listed in Table 7. In order to plot the relative enthalpy curve, it was necessary to decide on which enthalpy of fusion H_{fus} value to use. Different sources and studies mention different values of H_{fus} , a summary of which is available in Table 3. Because of the limited amount of experimental data available after the melting point, it was decided to use the value of 29.6 *KJ*/*mol* [15], as it matches the only found experimental data of relative enthalpy that was provided by the same source [15].

In this section, the outlier detection and the Unequal k-folds Cross Validation (UKFCV) methods will be used to give a statistical indication on which dataset should be dealt with as an outlier and therefore excluded from the assessment. The two methods used here are discussed in more detail in the work of Zomorodpoosh et al. [14] and Obaied [13].

6.1. Outlier detection method

In order to estimate which dataset should be excluded, the outlier detection method was developed as an automated tool that can be used to determine which of the datasets is not statistically coherent with the rest [13]. It was determined using this method that the dataset [34JAE] should be treated as an outlier. It is also important to reiterate that the dataset [88LIN] was excluded from the beginning as previously mentioned in section 2.1.

To further elaborate the steps taken in this method, the same dataset will be taken as an illustration example. First, all datasets were fitted with one of the datasets being excluded at a time, as shown in Fig. 17 for the case of the dataset [34JAE]. After that, the calculated relative enthalpy results were compared with experimental enthalpy datasets from the literature (see Fig. 18a) using statistical goodness of fit criteria as shown in Table 8. The difference of the relative enthalpy for the two compared cases can be seen in Fig. 18b. From these results, it is clear that excluding the [34JAE] dataset helped improving the goodness of fit of the heat capacity curve. The parameter values used for the MSR model before and after applying the outlier method are listed in Table 9.

6.2. Unequal K-Fold cross-validation (UKFCV) method

This method was developed to provide an automated tool to weight experimental or DFT data. It provides an automated assessment criterion for determining the weight of each dataset and detecting outlier. It is based on the k-fold cross-validation method, modified under the condition that each dataset contains an unequal number of observations. which is a typical situation during CALPHAD assessment. This method makes it possible to evaluate the reliability of each dataset involved in the assessment and to show the impact of weighting and outlier elimination on the statistical analysis results [14]. The UKFCV method was applied for pure Cr and the results can be seen in Fig. 19, where the MSR model results were plotted with and without weighting. The parameters values before and after assigning weights to the datasets can be seen in Table 10. The results obtained here are very similar to the ones obtained by the outlier detection method. But in addition to excluding the dataset [34JAE], it also excluded the dataset [27SIM]. It is worth mentioning here that the dataset [88LIN] was previously considered as an outlier and excluded before proceeding with the assessment as mentioned in section 2.1.

6.3. Comparison and final results

To further validate the MSR model results obtained for pure Cr, a comparison between the heat capacity, entropy and Debye temperature values from the literature and the values obtained after applying the outlier detection and UKFCV methods are listed in Table 11.

A summary of the heat capacity, relative enthalpy, entropy and Gibbs energy descriptions using the MSR model, with the algebraic function, for pure Cr can be seen in Fig. 20.

7. Conclusion

In this work, a modified version of the physically-based SR model for the description of thermodynamic properties of pure elements was proposed and applied for the case of pure Cr. A comprehensive literature review of pure Cr was followed by a model comparison to choose the most statistically accurate model for pure Cr from 0 K until the melting point, which was found to be the SR model. Then, two forms (simple and algebraic) of the sigmoid function were used to extend the SR model description of pure Cr beyond the melting point. Both methods showed results that allowed the SR model to become even more accurate and robust. The TDB file was successfully produced using the algebraic form of the sigmoid function, and it is expected that the simple form results can find potential applications when applied in other software.

Finally, two newly developed machine learning tools were used to calculate the weights of the datasets used in this assessment and detect potential outliers. It was concluded from both methods that the dataset [34JAE] should be removed from the assessment. In addition, the dataset [27SIM] was excluded by the UKFCV method. Since the two datasets are the oldest used in this assessment, it can be expected that the experimental measurement techniques used to produce the data back then were not as accurate as the data produced by other experimental efforts almost 30–50 years later. It is even mentioned in the publication by Jaeger et al. [81] where the dataset [34JAE] was taken from that the heat capacity formula was not included in the publication because there was still room for technical improvements in the calorimeter. For that reason it was decided to exclude these two datasets and treat them as outliers.

It is shown that the mathematical tools proposed and used in this work can offer a significant advantage to researchers developing new models, as they provide more flexibility to their designed models, as well as more accuracy when selecting potential datasets for their assessments.

8. Data availability

The raw data required to reproduce these findings are available to download from [https://doi.org/10.17632/rg8bw854yz.1]. The TDB file produced from this assessment is available to download from [https://doi.org/10.17632/tgbpyr58bm.1].

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