

The rational approximation method in the prediction of thermodynamic properties for SOFCs

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Abstract

The aim of this work is to present the method of rational approximation as an alternative technique for finding empirical models for thermophysical properties of relevant fluids to solid oxide fuel cells (SOFCs). The method of rational approximation is used here for calculating the isobaric heat capacity, the entropy of formation, the enthalpy, the Gibbs energy of formation, the thermal conductivity and the dynamic viscosity, at 0.1 MPa, of important gases in SOFCs (CH_4 , C_2H_6 , C_3H_8 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CO_2 , CO , H_2 , H_2O , O_2 , N_2 , NH_3). Rational approximations are well known for their ability to extrapolate, and this has been the main reason for adopting the method in this paper, since it is often difficult and expensive to have experimental data in the entire range of interest. A data survey was conducted for collecting the required information, and finally 75 rational approximations were generated all with a coefficient of determination of $R^2 = 99\%$.

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1. Introduction

A fuel cell is a device that transforms chemical energy into electricity. The energy stored in the fuel, usually hydrogen (H_2), is converted to electricity by the means of electrochemical reactions, the same principle found in a battery, with the difference being that a fuel cell operates as long as the fuel is supplied to the cell, whereas the battery is subject to a limited amount of fuel. One advantage of solid oxide fuel cells (SOFCs) over other types of fuel cells is the high operating temperature (700–1200 K), allowing for cogeneration and better efficiencies. This feature and the fact that all components are solids, make SOFCs very attractive for stationary applications. The Energy and Environmental Research Center (EERC) and the Chemical Engineering Department at the University of North Dakota are conducting a research in SOFCs and gasification processes, with the final goal of incorporating them together in a self-contained device. As part of this research the SOFC modelling is also in development. Modelling has become the main tool in understanding the complex behavior that

the fuel cell undergoes in operation; it is also used as a design tool. Many papers have been published in the literature, covering simple 2D steady models, e.g. [1,2], elaborated 3D transient models, e.g. [3–6], exergy–energy analysis, e.g. [7–10], and neural networks, e.g. [11,12]. All these models require reliable thermophysical properties often in the form of empirical correlations. Unfortunately, these properties are usually in tabulated form; if the experimental data is available. Just recently some researches [13] have started the task of compiling this information in to empirical correlations (polynomials) easy to implement in computational models. However, polynomial approximation often requires an extensive number of data points and high order polynomials (i.e. many fitting parameters) for generating good fits. Polynomial approximation gives poor results when is used for extrapolation, therefore its applicability is restricted to the data range. It would be better to have empirical correlations valid in a broader range, generated with few data points, and with less fitting parameters, but without sacrificing accuracy. Rational approximations usually require less data than polynomials for achieving the same results and they are good in representing complicated structures for interpolation and extrapolation. The method of rational approximation has been widely used in physics and mathematics, e.g. [14–17], but rarely in engineering areas. Hopefully, this work will

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start the interest on the technique, which is simple yet powerful.

Section 2 gives a brief description of the rational approximation technique for curve fitting. The results and final remarks are presented in Sections 3 and 4. Appendix A contains a guideline for those who want to write their own code in rational approximations.

2. Rational approximation

A rational approximation is the ratio of two polynomials $R(x) = P(x)/Q(x)$.

$$R(x) = \frac{\sum_{i=0}^N a_i x^i}{\sum_{i=0}^M b_i x^i}. \quad (1)$$

We can take $b_0 = 1$ without loss of generality, the resulting rational approximation is known as a Padé approximant of grade $[N/M]$ [18]. The goal when using rational approximation, or any other curve fitting technique is to find an empirical equation (correlation) such that the error difference between the original data points and the correlation is minimum. The most used method to minimize this error is known as the least squares error (LSE). For a rational approximation the LSE is expressed by

$$\text{LSE} = \sum_{i=1}^k \left(f_i - \frac{\sum_{j=0}^N a_j x_i^j}{1 + \sum_{j=1}^M b_j x_i^j} \right)^2, \quad (2)$$

$$\frac{\partial(\text{LSE})}{\partial a_j} = 0, \quad (3)$$

$$\frac{\partial(\text{LSE})}{\partial b_j} = 0, \quad (4)$$

where k is the number of data points, and (x_i, f_i) are the pairs of experimental data points; for example the data points obtained from measuring the isobaric heat capacity (f_i) at different temperatures (x_i).

The equations above will produce nonlinear results. An alternative linear form can be developed when the Cauchy–Padé method is used (see [14]),

$$f_i \approx \frac{P(x_i)}{Q(x_i)} \Rightarrow f_i Q(x_i) = P(x_i), \quad (5)$$

$$\text{LSE} = \sum_{i=0}^k A f_i Q(x_i) - P(x_i)^2, \quad (6)$$

$$\frac{\partial(\text{LSE})}{\partial a_i} = 0, \quad (7)$$

$$\frac{\partial(\text{LSE})}{\partial b_i} = 0. \quad (8)$$

Solving Eqs. (6)–(8) will generate a square matrix of coefficients, which can be solved using conventional linear

algebra techniques: LU decomposition, Gauss elimination, etc. Software packages such as Mathematica, and Maple incorporate rational approximations, but they are intended for the approximation of functions rather than data points. The curve fitting toolbox of MatLab is an excellent application for curve fitting, it includes rational, polynomial and many other methods. However, we decided to write our own code; detailed information is found in Appendix A.

3. Results

As reported in [19] the most probable options of fuels for SOFCs are: methane (CH_4), methanol (CH_4O), ethanol ($\text{C}_2\text{H}_6\text{O}$) and gasoline. However, gasoline is discarded in this study because of its non-renewable nature. Other important fluids are (see [13]): propane (C_3H_8), ethane (C_2H_6), steam (H_2O), carbon dioxide (CO_2), carbon monoxide (CO), nitrogen (N_2), oxygen (O_2) and hydrogen (H_2). Recently, ammonia (NH_3) has received some attention as an alternative fuel for SOFCs [20], and is also considered in this paper.

The residual plots, the average of the absolute deviation (AAD), the coefficient of determination R^2 , and the root mean squared error (RMSE) were used as indicators of the goodness of our correlations. However, just the R^2 is reported in the tables because is the most identifiable statistic. A great discussion on this topic and other ways to validate empirical models is found in [21],

$$\text{AAD} = \frac{1}{k} \sum_{i=1}^k \frac{|f_i - R(x)|}{f_i}, \quad (9)$$

$$R^2 = 1 - \frac{\sum_{i=1}^k (f_i - R(x))^2}{\sum_{i=1}^k (f_i - \bar{f})^2} = 1 - \frac{\text{SSE}}{\text{SST}}, \quad (10)$$

$$\text{RMSE} = \left(\frac{\text{SSE}}{k - (N + M + 1)} \right)^{1/2}, \quad (11)$$

$$\bar{f} = \frac{1}{k} \sum_{i=1}^k f_i. \quad (12)$$

A R^2 closer to 1 and RMSE closer to 0 indicate better fits.

3.1. Extrapolation with a small experimental sample

As mentioned before, rational approximation is useful when experimental data is scarce and extrapolation is needed. Two examples showing these features are discussed next. For the first example a Padé approximant was calculated for the isobaric heat capacity of methane, seventeen data points were used; the values were taken from the JANAF tables [22] in the range from 200–1500 K. The resulted correlation fitted the data with a $R^2 = 99.99\%$ and $s = 0.062$. Then, the approximation was compared with the equivalent polynomial expression reported in [13]. The

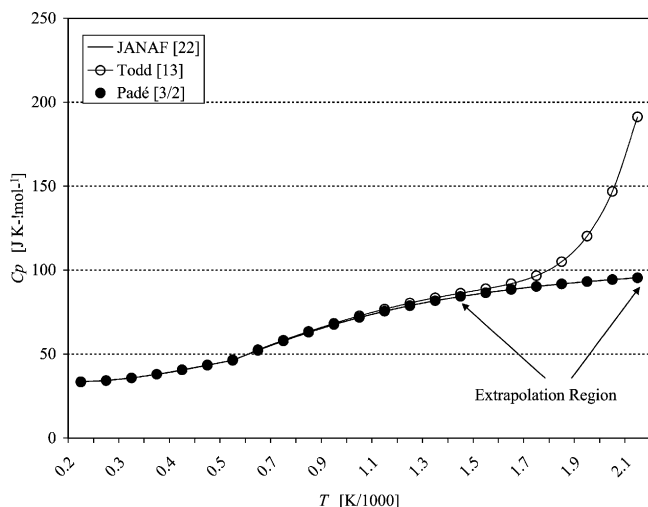


Fig. 1. Extrapolation to the isobaric heat capacity of methane using a Padé correlation generated with seventeen data points (●) and a polynomial correlation (○) reported by Todd and Young [13]. The estimation is compared to the experimental data reported in the JANAF tables [22].

Padé approximant, was able to fit the data over the interpolating range (200–1500 K) and the extrapolating range (1500–2000 K) as well (see Fig. 1). Also, the resulting correlation fitted the data with less fitting parameters than the expression in [13], but without losing accuracy. In the second example a Padé approximant was calculated for the isobaric heat capacity of carbon dioxide, but in this case just seven points were used, the resulting approximation fitted the data with a $R^2 = 99.99\%$ and $s = 0.0125$. The results are shown in Fig. 2. These examples show the ability to extrapolate data even when few experimental points were available. However, careful analysis is always recommended if the resulting approximation is intended for extrapolation.

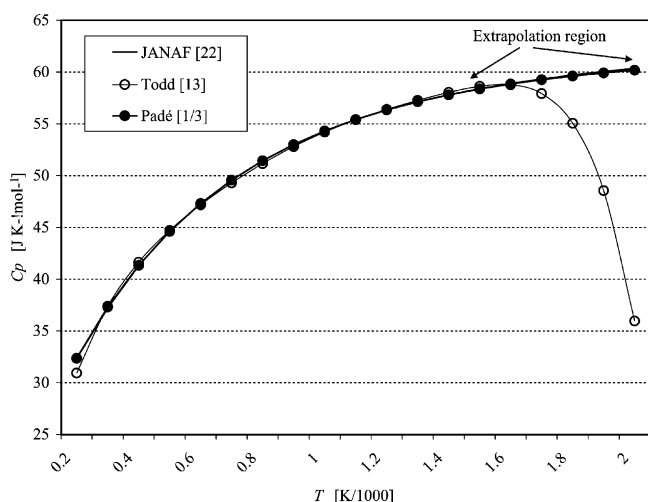


Fig. 2. Extrapolation for the isobaric heat capacity of carbon dioxide using a Padé correlation generated with seven data points (●) and the equivalent polynomial (○) reported by Todd and Young [13]. The estimation is compared to the experimental data reported in the JANAF tables [22].

3.2. Thermophysical properties

Padé correlations were computed for twelve fluids of interest in SOFCs. The thermophysical properties considered were the isobaric heat capacity (C_p), the entropy of formation (S°), the enthalpy of formation ($\Delta_f H^\circ$), the enthalpy, the Gibbs free energy of formation ($\Delta_f G^\circ$), the dynamic viscosity (μ) and the thermal conductivity (λ). The information was collected from published recommended data. We decided to use only experimental reported data, theoretical estimations and combination of two data sets (for enhancing the data set) was always avoided. Table 1 gives details about the sources consulted, it also gives the maximum temperature (T_{\max}) used in the generation of the Padé correlations. These equations could be used for extrapolation, if rough estimations are required, but not recommended for accurate estimations. Table 2 presents the absolute deviation, from the original data source, for the isobaric heat capacity (C_p), the viscosity (μ) and the thermal conductivity (λ). SOFCs operate usually between 800 and 1500 K, hence these two temperatures were chosen in Table 2. When this comparison was not possible, the closer temperature was reported, and it is indicated by a superscript. Also, when the experimental data was not available, extrapolation was used, and the comparison was made to other estimations reported in the literature, the references consulted for these comparisons are reported in the table as well. The thermophysical properties reported in Tables 3–14 and 16, follow the conventional form of a Padé approximant (see Eq. (1)). The Padé's grade [N/M] is included in each table. The tables report the coefficients from left to right as: $a_0, a_1, \dots, a_N, b_1, b_2, \dots, b_M$. Padé approximants are advantageous in the sense that can be generated with few experimental data points, and to some extent can be used for extrapolation. All the correlations reported had a coefficient of determination of $R^2 = 99\%$, and in many cases even better.

The enthalpy of formation at standard conditions ($\Delta_f H_{\text{Tr}}^\circ$) is reported in Table 15, the values reported in the JANAF tables are compared to the estimated values from the Padé correlations. The enthalpy (H°) is reported in Table 16, the reason is separated from the other properties is because the structure of the correlations is a bit different in the sense that it includes the term $\Delta_f H_{\text{Tr}}^\circ$. The Padé correlations for the enthalpy follow the same general form of Eq. (1) with the following modification:

$$H^\circ(T) = \frac{\sum_{i=0}^N a_i x^i}{1 + \sum_{i=1}^M b_i x^i} - \Delta_f H_{\text{Tr}}^\circ, \quad (13)$$

where $\text{Tr} = 298.15 \text{ K}$.

3.3. Discussion

For some fluids the deviation was more noticeable at lower temperatures. The residual plot is a good indicator to see if the correlation could be improved, when the plot is

Table 1
 T_{\max} used for interpolation and reference data

	C_p (J K ⁻¹ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)	$\Delta_f H^\circ$ (kJ mol ⁻¹)	$\Delta_f G^\circ$ (kJ mol ⁻¹)	μ (μPa s)	λ (mW m ⁻¹ K ⁻¹)	Reference
CH ₄	2000	2000	2000	2000	1773	1773	[22–24]
C ₂ H ₆	1500	1500	1500	1500	1773	600	[23,25,26]
C ₃ H ₈	1500	1500	1500	1500	750	600	[25–27]
CH ₃ OH	1500	1500	1500	1500	600	750	[25,27–29]
C ₂ H ₅ OH	1500	1500	1500	1500	600	1000	[25,27,29]
CO ₂	2000	2000	2000	2000	1500	1400	[22,24,28,30]
CO	2000	2000	2000	2000	1773	2000	[22,23,31]
H ₂	2000	2000	–	–	2000	2000	[22,32,28]
H ₂ O	2000	2000	2000	2000	1073	1073	[22,33]
O ₂	2000	2000	–	–	1400	1400	[22,34]
N ₂	2000	2000	–	–	1773	2000	[22,23,31]
NH ₃	2000	2000	2000	2000	850	850	[22,35]

$T_{\min} = 298.15$ K for all cases.

Table 2
 Deviation (%) at $T_1 = 800$ K and $T_2 = 1500$ K with respect to the source data

	C_p		μ		λ		Reference
	T_1	T_2	T_1	T_2	T_1	T_2	
CH ₄	0.0223	0.0086	0.04020	0.0027 ^a	0.0424	0.0006 ^a	
C ₂ H ₆	0.0078	0.0010	0.00420	0.0022 ^a		NA	[13]
C ₃ H ₈	0.0677	0.0289	0.2046 ^b	NA		NA	[13]
CH ₃ OH	0.0600	0.0092	0.6722 ^c	NA	0.7029 ^b	NA	[36]
C ₂ H ₅ OH	0.0754	0.0369	1.5425 ^c	NA	0.0434	NA	[36]
CO ₂	0.0161	0.0202	0.00530	0.00470	0.2415	0.1860 ^d	
CO	0.0444	0.0060	0.00010	0.0007 ^a	0.0064	0.0189	
H ₂	0.0942	0.0172	0.08710	0.05410	0.3170	0.3311	
H ₂ O	0.0619	0.0090	0.00300	5.3334 ^c	0.0009	1.7058 ^c	[13]
O ₂	0.2799	0.0220	0.00130	0.0028 ^d	0.0848	0.0823 ^d	
N ₂	0.0877	0.0501	0.00010	0.0007 ^a	0.0206	0.0177	
NH ₃	0.1325	0.0079	0.01150	NA	0.0447	NA	

^a $a = 1773$ K.

^b $c = 750$ K.

^c Extrapolation.

^d $b = 1400$ K.

Table 3
 Thermophysical properties for methane (CH₄)

	[N/M]							R^2
C_p	[3/2]	44.300100	−0.076325770	0.0004250204	−2.003423E−08	0.0013033600	2.889771E−06	0.9999
S°	[1/3]	141.046300	0.408253200	0.0014772460	−3.113396E−07	5.277425E−11		0.9999
$\Delta_f H^\circ$	[2/3]	−68.316570	−0.022445170	−0.0001987408	0.0002184224	1.917568E−06	8.629875E−11	0.9999
$\Delta_f G^\circ$	[3/2]	−69.418760	−0.054269370	6.414136E−05	1.284521E−07	0.0013455240	1.191685E−06	0.9999
μ	[3/1]	−1.217438	0.052877710	2.023846E−05	−3.791026E−10	0.0015520230		0.9999
λ	[2/2]	11.632370	−0.006260186	0.0004209756	0.0011157170	3.14901E−070		0.9999

Table 4
 Thermophysical properties for ethane (C₂H₆)

	[N/M]							R^2
C_p	[2/2]	12.735040	0.12691270	0.0001646422	0.0005393203	9.430913E−07		0.9999
S°	[2/1]	173.096400	0.24741290	−5.128808E−06	0.0002526365			0.9999
$\Delta_f H^\circ$	[2/2]	−64.795130	−0.09806924	−2.056518E−05	0.0003588526	3.861861E−07		0.9999
$\Delta_f G^\circ$	[1/3]	−79.384720	0.16901950	−0.0003939651	2.669346E−07	−6.403402E−11		0.9999
μ	[2/1]	−1.933514	0.04468533	1.181946E−05	0.0011285110			0.9999
λ	[3/2]	−1.778584	0.07049372	−0.0002124490	9.348156E−07	−0.0009316998	5.311781E−06	0.9999

Table 5
Thermophysical properties for propane (C₃H₈)

	[N/M]							R ²
C _p	[2/2]	12.350270	0.17762730	0.0004986025	0.0010922370	1.849955E-06		0.9999
S ^o	[1/2]	190.485800	0.33304640	0.0002374546	1.724174E-08			0.9999
Δ _f H ^o	[1/2]	-76.440570	-0.15892480	0.0005722084	2.468723E-07			0.9999
Δ _f G ^o	[2/3]	-95.345180	0.19314520	0.0001473752	0.0001054764	2.275926E-07	-5.275657E-11	0.9999
μ	[1/2]	1.559428	0.01903184	-0.0005999190	5.891039E-07			0.9999
λ	[2/2]	3.074473	-0.01341112	0.0002030202	-0.0004190028	9.777090E-07		0.9999

Table 6
Thermophysical properties for methanol (CH₃OH)^a

	[N/M]							R ²
C _p	[2/2]	27.2063700	0.033667820	0.0002323243	0.0005524408	1.718860E-06		0.9999
S ^o	[1/2]	191.6626000	0.289763300	0.0005418806	-2.739696E-08			0.9999
Δ _f H ^o	[1/2]	-185.5023000	-0.187439200	0.0006556361	6.370553E-08			0.9999
Δ _f G ^o	[1/3]	-197.1941000	0.146381600	-0.0002355756	2.000135E-07	-5.928055E-11		0.9999
μ ^a	[1/1]	-0.7339101	0.036183810	0.0001126046				0.9997
λ ^a	[1/3]	3.6246360	0.006034229	-0.0034030690	4.583233E-06	-2.179021E-09		0.9996

^a T_{min} = 340 K.

Table 7
Thermophysical properties for ethanol (C₂H₅OH)^a

	[N/M]							R ²
C _p	[2/2]	37.5630800	0.003701471	0.0010894790	0.0021285390	4.834939E-06		0.9999
S ^o	[2/1]	208.3071000	0.365999500	6.727513E-06	0.0004345229			0.9999
Δ _f H ^o	[1/3]	-213.6227000	-0.171063100	0.0003840254	1.479425E-07	-2.149535E-11		0.9999
Δ _f G ^o	[2/3]	-221.0303000	-0.422576100	0.0006763252	0.0023520990	9.009738E-08	-1.213238E-11	1.0000
μ ^a	[1/1]	-0.3081893	0.032087770	0.0001755315				0.9986
λ ^a	[1/3]	-3.5346540	0.043296920	-0.0016633990	1.461276E-06	-4.922065E-10		0.9999

^a T_{min} = 360 K.

Table 8
Thermophysical properties for carbon dioxide (CO₂)

	[N/M]							R ²
C _p	[1/3]	15.9293400	0.1310897000	0.0015818570	1.413140E-07	-1.492641E-11		0.9999
S ^o	[1/3]	162.2327000	0.4991412000	0.0015669680	-1.272666E-07	1.590139E-11		0.9999
Δ _f H ^o	[0/4]	-393.5301000	2.955723E-06	-9.660127E-09	4.875419E-12	-9.033876E-16		0.9996
Δ _f G ^o	[3/1]	-393.3602000	-0.0668642900	1.063131E-06	-3.307527E-11	0.0001599438		0.9998
μ	[2/3]	-0.3627303	0.0493084000	0.0001247949	0.0019321880	1.480674E-06	-2.024057E-10	0.9999
λ	[1/3]	-2.7993020	0.0537140700	-0.0009294698	9.780868E-07	-3.028957E-10		0.9999

Table 9
Thermophysical properties for carbon monoxide (CO)

	[N/M]							R ²
C _p	[3/2]	29.688350	-0.03756144	5.373678E-05	1.170652E-09	-0.0011319600	1.549482E-06	0.9999
S ^o	[1/3]	126.590700	1.40057800	0.0060710860	-6.607275E-07	1.024591E-10		0.9999
Δ _f H ^o	[3/1]	-114.807900	-0.18031910	-2.255532E-05	1.685088E-09	0.0018228270		0.9998
Δ _f G ^o	[3/2]	-110.472500	-0.03484187	6.937390E-06	-2.724657E-08	-0.0004932971	3.203531E-07	0.9999
μ	[2/3]	-7.186509	0.14984760	0.0005861958	0.0118500000	5.491016E-06	-8.945480E-10	0.9999
λ	[2/3]	-2.279536	0.11057870	5.884957E-05	0.0015509920	-2.176592E-07	6.198217E-11	0.9999

Table 10
Thermophysical properties for hydrogen (H₂)

	[N/M]							R ²	
C _p	[4/2]	24.130810	0.001107916	2.723492E-05	3.707239E-08	-5.867667E-12	-0.0008902458	2.660622E-06	0.9981
S°	[2/2]	74.709380	0.677136600	0.0001220837	0.0039266450	3.303912E-07			0.9999
μ	[2/1]	2.251621	0.027411680	8.300364E-06	0.0008476300				0.9999
λ	[1/3]	-13.500230	0.967976900	0.0020700670	-1.166006E-06	2.138789E-10			0.9999

Table 11
Thermophysical properties for water (H₂O)

	[N/M]							R ²
C _p	[2/2]	33.253760	-0.007235433	3.047110E-05	-0.0001375154	5.058140E-07		0.9999
S°	[1/3]	119.670700	1.058446000	0.0045406960	-5.492381E-07	7.037198E-11		0.9999
Δ _f H°	[2/1]	-238.039200	-0.073690040	2.072838E-06	0.0002495145			0.9995
Δ _f G°	[1/2]	-241.365800	0.044332430	-1.770163E-05	4.030592E-08			0.9999
μ	[1/2]	-1.043642	0.031849010	-0.0003785168	1.976538E-07			0.9999
λ	[2/1]	31.182260	-0.111481900	0.0004250616	0.0025513490			0.9999

Table 12
Thermophysical properties for oxygen (O₂)

	[N/M]							R ²
C _p	[3/2]	28.057060	-0.04059181	2.917448E-05	4.033074E-09	-0.0015852160	1.177089E-06	0.9990
S°	[2/1]	159.823000	0.59264270	2.580317E-05	0.0021935650			0.9999
μ	[2/3]	-3.008213	0.11590190	0.0001831793	0.0041151080	1.046158E-06	-1.285754E-10	0.9999
λ	[2/1]	2.551594	0.08442653	-2.148324E-06	0.0002034283			0.9999

Table 13
Thermophysical properties for nitrogen (N₂)

	[N/M]							R ²	
C _p	[2/2]	29.418560	-0.02399357	3.523777E-05	-0.0007104165	9.562046E-07		0.9996	
S°	[3/1]	117.768500	1.53470400	0.0002048388	-2.673700E-08	0.0070239710		0.9999	
μ	[2/3]	-7.186509	0.14984760	0.0005861958	0.0118500000	5.491016E-06	-8.945480E-10	0.9999	
λ	[2/4]	-18.588180	0.32766320	0.0005955238	0.0152286000	-5.872769E-06	3.342142E-09	-6.129376E-13	0.9999

Table 14
Thermophysical properties for ammonia (NH₃)

	[N/M]							R ²
C _p	[2/2]	30.183570	0.01828932	7.105129E-05	0.0003203040	7.942573E-07		0.9999
S°	[1/3]	134.846000	0.72763790	0.0029158910	-4.892336E-07	7.254739E-11		0.9999
Δ _f H°	[2/2]	-38.172200	-0.04001909	-7.888714E-06	0.0002634952	3.009345E-07		0.9999
Δ _f G°	[2/2]	-41.502500	-0.01514588	0.0002335444	0.0018138650	4.466832E-08		0.9999
μ	[2/3]	8.622304	-0.04270181	0.0003155012	0.0030816200	5.585175E-06	-1.871846E-09	0.9999
λ	[4/1]	33.485680	-0.13574630	0.0002697936	5.944465E-07	-7.579975E-10	0.0002611385	0.9999

Table 15
Enthalpy of formation at standard temperature

Fluid	JANAF	Padé	Dev _a
CH ₄	-74.8730	-74.8668	0.0082
C ₂ H ₆	-84.0000	-83.9926	0.0088
C ₃ H ₈	-103.8470	-103.8314	0.0150
CH ₃ OH	-201.0000	-200.9650	0.0174
C ₂ H ₅ OH	-234.8000	-234.7886	0.0049
CO ₂	-393.5220	-393.4732	0.0124
CO	-110.5270	-110.4847	0.0383
H ₂ O	-241.8260	-241.8349	0.0037
NH ₃	-45.8980	-45.8958	0.0049

Δ_fH° (298.15 K).

randomly scattered around zero the approximation can not be improved, otherwise a better correlation can be generated. For example, the C_p of hydrogen could be improved if a Padé [4/3] is used instead of a Padé [4/2] (see Fig. 3). However, since SOFCs operate at high temperatures, we decided to stay with the simpler Padé for this and similar cases. The absolute deviation (Dev_a) is defined as

$$\text{Dev}_r = \frac{f_i - R(x_i)}{f_i} \times 100,$$

$$\text{Dev}_a = |\text{Dev}_r|.$$

Table 16
Padé [N/M] correlations for predicting the enthalpy

Fluid									R^2
CH ₄	[5/1]	-85.75843	-0.08219566	-2.205121E-05	1.511815E-07	-6.524674E-11	1.178606E-14	0.0015155080	0.9999
C ₂ H ₆	[1/4]	-93.89374	0.08138350	-0.0007150031	5.329930E-07	-2.122816E-10	3.441019E-14		0.9999
C ₃ H ₈	[1/5]	-117.15270	0.11008020	-0.0007993322	6.300195E-07	-2.104673E-10	-1.898936E-14	2.039528E-17	0.9999
CH ₃ OH	[4/1]	-208.60450	-0.32474160	9.307114E-05	5.880019E-08	-1.189421E-11	0.0015801140		0.9999
C ₂ H ₅ OH	[2/3]	-245.92480	-0.04058813	8.462722E-05	0.0001911241	1.206822E-07	-3.202532E-11		0.9999
CO ₂	[2/2]	-402.53190	-0.18356540	2.532474E-05	0.0005100149	4.714306E-08			0.9999
CO	[5/1]	-120.34680	-0.06796633	-7.965714E-06	4.959540E-08	-2.876021E-11	6.574728E-15	0.0009008641	0.9999
H ₂ O	[3/2]	-252.19510	0.06739300	-0.0001262354	2.291166E-08	-0.0001250512	4.599617E-07		0.9999
NH ₃	[1/5]	-55.27327	0.04514227	-0.0003096372	-2.741745E-09	1.673412E-10	-1.182764E-13	2.740371E-17	1.0000

Although, all thermophysical properties were represented with rational approximations, some properties could be correlated with simpler techniques, such as polynomial or linear regression. Our intention is to present the method as an alternative, but the decision as to be taken based on the structure of the data (simple or complicated), the number of experimental points available, and the needs for the resulting correlation (interpolation or extrapolation). Finally, is important to mention that there are some empirical correlations for thermophysical properties, that are remarkably simple and powerful. Some of these are the viscosity and thermal conductivity for many liquids and gases reported in [36], or in the case of the heat capacity, the correlations reported in [37]. These correlations give good estimations, but not necessarily the best. Fig. 4 compares the absolute deviation to the JANAF tables of the Padé correlations reported here, and the empirical correlations reported in [37] at 1500 K. Although both gave very good results, the Padé correlations seem to be more consistent in reporting always the smaller deviation. However, this could be due to the fact that different data sets were used in generating the correlations. In fact, He et al. [38] report these incon-

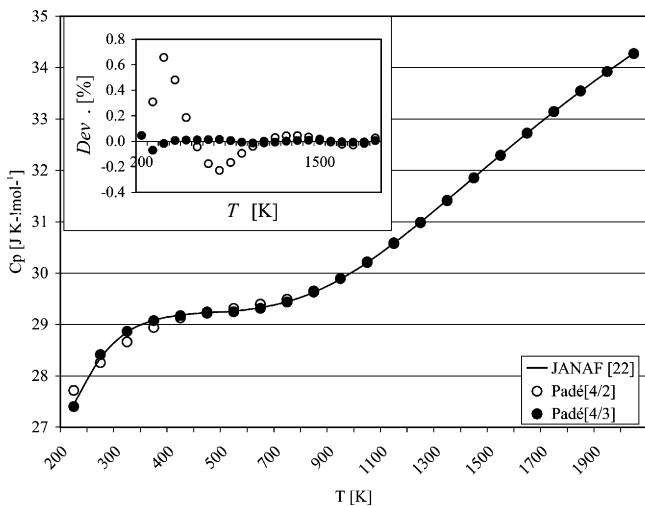


Fig. 3. Approximation to the isobaric heat capacity of hydrogen using a Padé correlation of order [4/2] (○) and the improved Padé correlation of order [4/3] (●).

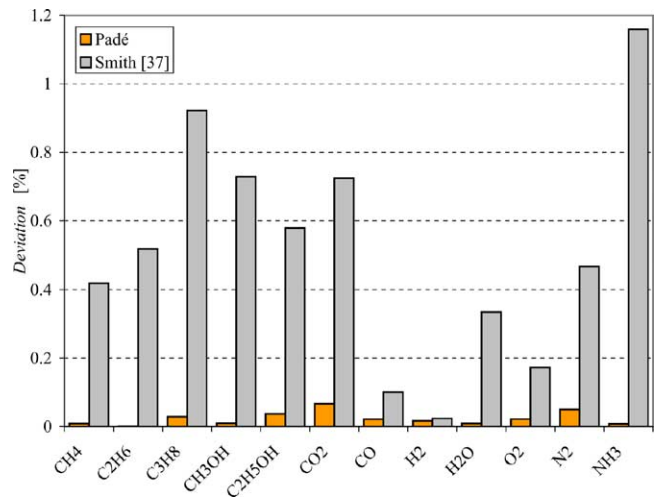


Fig. 4. Comparison between the estimation of the isobaric heat capacity at 1500 K, using Padé correlations and the equations reported in by Smith et al. [37].

sistencies in compiling thermodynamic data from different sources.

The Padé correlations usually produce good results with few experimental points, are good candidates for extrapolation and are capable of fitting complicated structures. However, they tend to become unstable at the poles (zeros in the denominator) of the function and sometimes the approximation does not converge. Special care to this matter is recommended.

4. Final remarks

The method of rational approximation was successfully used in the representation of the thermophysical properties for relevant fluids to SOFCs. The method was used for extrapolation when little experimental data was available. This was the case for ethane, propane, methanol and water. The extrapolated estimation was compared with estimations reported by others. All 75 correlations had a $R^2 = 99\%$. The correlations reported in this paper generally required less fitting parameters than the polynomials by Todd and Young

[13]. Some correlations were not able to fit the data very well at low temperatures. Residual plots showed that these approximations could be improved, however, since SOFCs operate between 800 and 1500 K, we decided to report simpler correlations that worked better at high temperatures. Polynomials are very good interpolating experimental data, but not for extrapolation, and this has been the main reason for adopting rational approximations. However, analytic integration is more difficult for rational approximations, thus calculating enthalpies or entropies using the correlations for the C_p is not as easy as with polynomials, and this is why we are reporting independent correlations for these thermodynamic properties. The correlations presented in this paper were created having the modelling of SOFCs in mind. During the operation of SOFCs it is sometimes difficult to have a perfect control in the variables involved and temperatures rise above the expected values. If this is the case a polynomial representation could lead to an incorrect analysis of the system. Rational approximations due to their ability to extrapolate, will not be as susceptible to these operational changes.

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Appendix A

An example is developed to clarify the method. Let's assume that a rational approximation is required to fit a k number of data points with three coefficients; Padé [1/1]. The Padé approximant will be then

$$R(x) = \frac{\sum_{i=0}^{N=1} a_i x^i}{1 + \sum_{j=1}^{M=1} b_j x^j} = \frac{a_0 + a_1 x}{1 + b_1 x}. \quad (\text{A.1})$$

In order to find the coefficients in (A.1) the least squares method is used, the resulting equations are

$$\text{LSE} = \sum_{l=1}^k \left(f_l + \sum_{j=1}^M b_j x^j - \sum_{i=0}^N a_i x^i \right)^2$$

$$\frac{\partial E}{\partial a_i} = 2 \sum_{l=1}^k \left(f_l \left(1 + \sum_{j=1}^M b_j x^j \right) - \sum_{i=0}^N a_i x^i \right) (x_l^i) = 0$$

$$\frac{\partial E}{\partial b_j} = 2 \sum_{l=1}^k \left(f_l \left(1 + \sum_{j=1}^M b_j x^j \right) - \sum_{i=0}^N a_i x^i \right) (f_l x_l^j) = 0$$

$$\begin{pmatrix} -3 & -\sum x_i & \sum f_i x_i \\ -\sum x_i & -\sum x_i^2 & \sum f_i x_i^2 \\ -\sum f_i x_i & -\sum f_i x_i^2 & \sum f_i^2 x_i^2 \end{pmatrix} \times \begin{pmatrix} a_0 \\ a_1 \\ b_1 \end{pmatrix} = \begin{pmatrix} -\sum f_i \\ -\sum f_i x_i \\ \sum f_i^2 x_i \end{pmatrix} \quad (\text{A.2})$$

$$\mathbf{A} \times \mathbf{c} = \mathbf{b} \quad (\text{A.3})$$

where $\sum = \sum_{i=1}^{k=3}$.

The matrix can be solved using conventional techniques. Unfortunately, when more coefficients are required creating the matrix becomes more complicated. A pattern can be identified, the pattern is then broken in different sub-matrices.

1. \mathbf{A}_1 : elements of \mathbf{A} less than N in the rows and in the columns.
2. \mathbf{A}_2 : elements of \mathbf{A} less than N in the rows but greater than n in the columns.
3. \mathbf{A}_3 : elements of \mathbf{A} greater than N in the rows but less than n in the columns.
4. \mathbf{A}_4 : elements of \mathbf{A} greater than N in the rows and in the columns.
5. \mathbf{b}_1 : elements of \mathbf{b} less than N in the rows.
6. \mathbf{b}_2 : elements of \mathbf{b} greater than N in the columns.

where N is the numerator grade ($N = 1$ for the example above). The final matrix is build upon the integration of these sub-matrices. The equations for creating them are provided next,

$$\mathbf{A}_1 : \ell_{c,r} = -\sum_{i=1}^k x_i^{c+r}, \quad \mathbf{A}_2 : \ell_{c,r} = \sum_{i=1}^k f_i x_i^{c+r-N} \quad (\text{A.4})$$

$$\mathbf{A}_3 = -\mathbf{A}_2^T, \quad \mathbf{A}_4 : \ell_{c,r} = \sum_{i=1}^k f_i^2 x_i^{c+r-2N} \quad (\text{A.5})$$

$$\mathbf{b}_1 : \ell_r = -\sum_{i=1}^k f_i x_i^r, \quad \mathbf{b}_2 : \ell_r = -\sum_{i=1}^k f_i^2 x_i^{r-N} \quad (\text{A.6})$$

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{A}_3 & \mathbf{A}_4 \end{pmatrix} \quad \mathbf{b} = \begin{pmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \end{pmatrix} \quad (\text{A.7})$$

where c are the columns, r the rows and ℓ the coefficient elements.

Once the matrix is created is just a matter of finding \mathbf{A}^{-1} in (A.7). An algorithm in C or Fortran can be implemented readily, an excellent reference for solving (A.3) can be found in [39].

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- Editor's note: A technical update on Rational Approximations appears in this issue of J. Power Sources*
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