

HYDROGEN PRODUCTION USING A THERMOCHEMICAL CYCLE

PROIZVODNJA VODIKA S TERMOKEMIČNIM PROCESOM

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Abstract

Sustainable methods of clean fuel production are needed throughout the world due to depleting oil reserves and the need to reduce carbon dioxide emissions. The technology based on fuel cells for electricity production or the transport sector has already been developed. However, a key missing element is a large-scale method of hydrogen production. The copper-chlorine (CuCl) combined thermochemical cycle is a promising thermochemical cycle that can produce large amounts of cheap hydrogen. A particularly promising part of this process is its use in combination with nuclear or thermal power plants. This paper focuses on a CuCl cycle and describes the models used to calculate thermodynamic and transport properties. This paper discusses the mathematical model for computing the thermodynamic properties for pure HCl and CuCl₂.

The mathematical model developed for the solid phase takes into account vibrations of atoms in molecules and intermolecular forces. This mathematical model can be used for the calculation of the thermodynamic properties of polyatomic crystals on the basis of the Einstein and Debye equations. The authors of this paper developed the model in the low temperature and high temperature region. All the analytical data have been compared with some experimental results and show a relatively good match. For the solid phase, the authors developed a model to calculate thermal conductivity based on electron and phonon contributions.

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Povzetek

Zaradi izčrpavanja zaloga nafte in potrebe po zmanjšanju emisij ogljikovega dioksida so trajnostne metode proizvodnje čistega goriva potrebne v vseh državah sveta. Tehnologija na osnovi gorivnih celic je že razvita, vendar pa je ključni manjkajoči element obsežna proizvodnja vodika. Kombinirani termokemični cikel baker-klor (CuCl) predstavlja obetaven termokemični cikel za proizvodnjo poceni vodika v velikih količinah, kar je proces, ki je še posebej zanimiv v kombinaciji z jedrskimi elektrarnami ali termoelektrarnami. Ta članek se osredotoča na cikel baker-klor (CuCl) in opisuje modele, kako izračunati termodinamične in transportne lastnosti, pri čemer obravnava matematični model za izračun termodinamičnih lastnosti za čisti HCl in CuCl_2 .

Razvit matematični model za trdno fazo upošteva vibracije atomov v molekulah in medmolekulske sile. Ta matematični model, ki se lahko uporablja za izračun termodinamičnih lastnosti poliatomskih kristalov na podlagi Einsteinovih in Debyejevih enačb, smo razvili v nizkotemperaturnem in visokotemperaturnem območju. Analitične podatke smo primerjali z nekaterimi eksperimentalnimi rezultati in kažejo dobro ujemanje. Za trdno fazo smo razvili model za izračun toplotne prevodnosti na podlagi prispevkov elektronov in fononov.

1 INTRODUCTION

The ecological problems throughout the world are becoming significantly bigger by the year. One of the possible ways of reducing greenhouse gas emissions is the introduction of hydrogen technologies. However, the biggest problem is the production of large enough amounts of hydrogen. Hydrogen can be obtained from hydrocarbons, but it can also be obtained from water. This article deals with the extraction of hydrogen from water, which, from an ecological perspective, is a much more acceptable process than the extraction of hydrogen from coal, oil and natural gas. Water decomposes naturally into hydrogen and oxygen at 2,500°C. Therefore, in recent decades, thermochemical processes in laboratories have improved and electrolysis processes are also being improved. While the production of hydrogen in thermochemical processes mainly requires thermal energy, electricity is required for the electrolysis process. With the introduction of the new generation of nuclear reactors, where temperatures will be much higher than in existing reactors, the cogeneration of electricity and hydrogen [1-4] in connection with a nuclear power plant and thermochemical processes for hydrogen production can be a promising technology in the future.

2 THERMOCHEMICAL CYCLE FOR HYDROGEN PRODUCTION IN COMBINATION WITH A PWR NUCLEAR POWER PLANT

Rather than deriving hydrogen from fossil fuels, a promising alternative is the thermochemical decomposition of water [1]. Electrolysis is a proven commercial technology that separates water into hydrogen and oxygen using electricity. Net electrolysis efficiencies (including both electricity and hydrogen generation) are typically about 32%. In contrast, thermochemical cycles to produce hydrogen promise heat-to-hydrogen efficiencies of up to about 50%. Through thermochemical cycles, hydrogen is produced by chemical processes and heat supply at significantly lower temperatures than natural decomposition into hydrogen and oxygen. The temperatures usually necessary for thermochemical decomposition range between 750°C and 1,000°C (Table 1).

Table 1: A short description of the most tested thermochemical cycles [1-9]

Name of the cycle	Maximum temperature (°C)	Use efficiency (%)	Advantages	Reference
Sulphur-iodine	823-900	42-51	Use efficiency beyond 60% is also planned	[1]
UT-3 Calcium-bromine	750	40-50	Lower maximum temperature	[4]
Vanadium-chlorine	925	40.5-42.5		[4]
Hybrid Copper-chlorine cycle	550	46	Low maximum temperature	[4]
Hybrid copper-sulphur	827	68-73	High use efficiency	[1,4]

The aforementioned requirement for a relatively high temperature prevents the application of thermochemical cycles for conventional, water-cooled nuclear reactors. However, the use of high temperature gas-cooled reactors or fourth-generation reactors would be possible. The beginnings of research into the thermochemical cycles of hydrogen production from water date back to around 1960. The key advantage of thermochemical cycles over others is the high use efficiency, which, in some cycles, goes beyond 50%. The next great advantage over other cycles is the circular process, where the environmental strain caused by CO₂ is no longer a problem.

In scientific literature, there are more than 200 thermochemical cycles [2], the majority of which have never been tested as pilot projects. Most of these cycles are being developed in the USA, Japan, Canada and France. The following table displays the most well known thermochemical cycles: of particular interest are the thermochemical hybrid cycles, which, apart from waste heat, require electrical energy from a nuclear power plant to operate.

This article examines the thermophysical properties of a specific cycle called the copper-chlorine (CuCl) cycle, with particular relevance to nuclear-produced hydrogen. A conceptual schematic of the CuCl cycle is shown in literature [2,3]. In this cycle, water is decomposed into hydrogen and oxygen through intermediate CuCl compounds. Nuclear-based 'water splitting' requires an intermediate heat exchanger between a nuclear reactor and hydrogen plant, which transfers heat from the reactor coolant to the thermochemical cycle. An intermediate loop prevents exposure to radiation from the reactor coolant in the hydrogen plant, and also prevents corrosive fluids in the thermochemical cycle from entering the nuclear plant. Table 2 shows the most important components in the CuCl thermochemical process of hydrogen production.

Table 2: Fundamental thermophysical properties for selected CuCl components

	HCl	CuCl	CuCl ₂	Cu ₂ OCl ₂	CuO
	Hydrochloric acid	Cuprous chloride	Cupric chloride	Copper oxychloride	Cupric oxide
Molecular weight [kg/kmol]	36.5	98.9	134.5	214	79.54

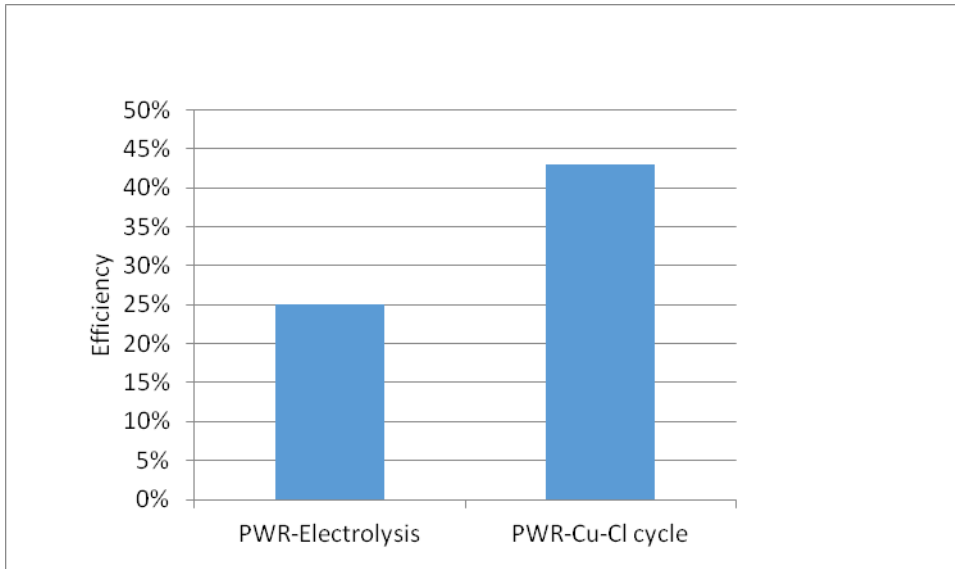


Figure 1: Total net efficiency for the production of hydrogen in comparison with electrolysis and a CuCl cycle

The production price of hydrogen was calculated in relation to the PWR nuclear power plant. The results are shown in Table 3, namely the price of hydrogen produced through electrolysis or using a CuCl process. The CuCl process was based on the assumption that 1 MWh of electricity costs EUR 35, while in terms of hydrogen production through electrolysis, it was assumed that 79 kWh of power (51% efficiency) is required. The price of thermal energy from a nuclear power plant was calculated from the Rankine process based on the assumption of steam consumption at the low-pressure stage of the turbine. Table 3 and Figure 3 show the prices calculated for hydrogen production, excluding investment costs.

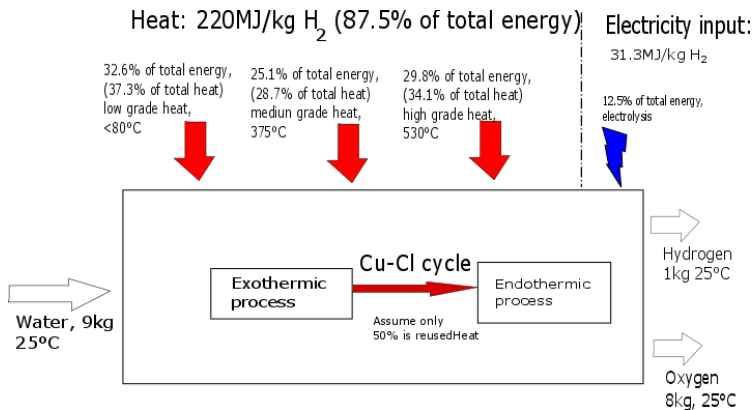


Figure 2: CuCl process energy requirements for process [5]

Table 3: Calculated prices for 1kg of hydrogen

Electrolysis	2.76 EUR/kg H ₂
CuCl thermochemical process	Electrical energy 0.3 EUR Price for heat at 80°C 0.233 EUR Price for heat at 400°C 0.217 EUR Price for heat at 600°C 0.315 EUR Total 1.065 EUR

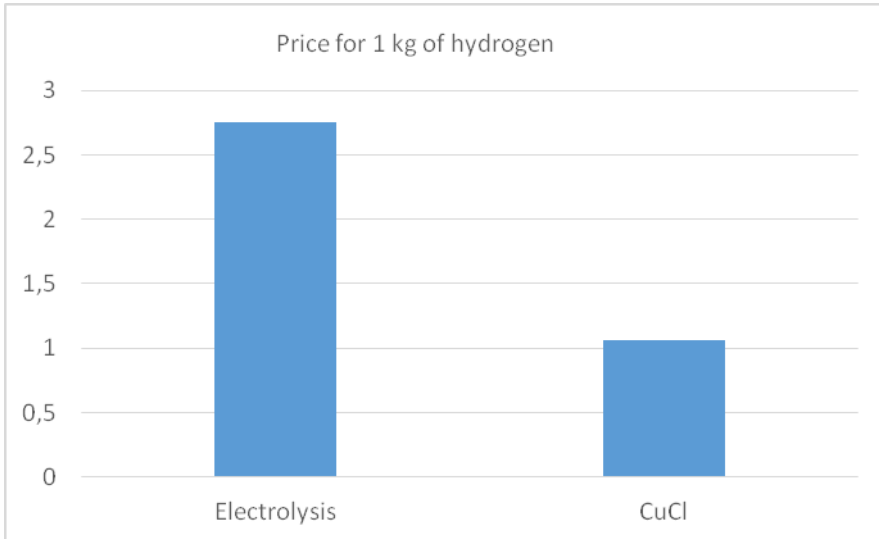


Figure 3: Comparison of hydrogen price

3 THERMODYNAMIC PROPERTIES FOR SOLIDS

In the theoretical formulation for solids it will be assumed that each form of motion of energy is independent of the others. Thus, the energy of the system of molecules can be written as a sum of the following individual contributions or decoupled forms of motion [2]:

- a) vibrational energy of molecules (E_{vib}), due to the relative motion of atoms inside the molecules
- b) potential energy (E_{pot}) of a system of molecules, which occurs due to the attractive or repulsive intermolecular forces in a system of molecules
- c) energy of electrons (E_{el}), which is concentrated in the electrons or the electron shell of an atom or a molecule
- d) nuclear energy (E_{nuc}), which is concentrated in the atom nucleus

The partition function is defined as Z [6-10], which is applied to the system of particles with a certain volume V , temperature T and particle number N . Assuming that the energy spectrum is

continuous, together with the other aforementioned assumptions, the canonical partition function for the one-component system can be expressed in the following manner [9]:

$$Z = \frac{1}{N! h^{Nf}} \int \dots \int \exp\left(-\frac{E_{vib} + E_{el} + E_{nuc}}{k_B T}\right) \cdot d\bar{p}_1 \cdot d\bar{p}_2 \dots d\bar{p}_N \int \dots \int \exp\left(-\frac{E_{pot}}{k_B T}\right) d\bar{r}_1 \cdot d\bar{r}_2 \dots d\bar{r}_N \quad (3.1)$$

The second term on the right-hand side of equation 3.1 is called the configurational integral, where f is the number of degrees of freedom of an individual molecule, p is momentum, r is the coordinate, and E_{vib} , E_{el} , E_{nuc} , and E_{pot} represent the vibrational energy, electron energy and nuclear energy of individual molecules, and the potential energy between two molecules respectively.

Similarly, the partition function Z for a multi-component system of indistinguishable molecules can be expressed as follows:

$$Z = \frac{1}{\prod N_i! h^{N_i f_i}} \int \dots \int \exp\left(-\frac{E_{vib} + E_{el} + E_{nuc}}{k_B T}\right) d\bar{p}_1 \cdot d\bar{p}_2 \dots d\bar{p}_N \cdot \int \dots \int \exp\left(-\frac{E_{pot}}{k_B T}\right) d\bar{r}_1 \cdot d\bar{r}_2 \dots d\bar{r}_N \quad (3.2)$$

In equation 3.2, N_i is the number of molecules of the i -th component, while f_i is the number of degrees of freedom of the i -th molecule. Using the canonical partition, the partition function Z of the one-component system as a product of partition functions becomes:

$$Z = Z_g Z_{vib} Z_{el} Z_{nuc} Z_{conf} \quad (3.3)$$

The partition function Z is a product of terms of the ground state (g), translation ($trans$), vibration (vib), rotation (rot), internal rotation (ir), influence of electron excitation (el), influence of nuclei excitation (nuc) and the influence of the intermolecular potential energy ($conf$). Utilising the canonical theory for computing the thermodynamic functions of the state leads to:

$$\text{Pressure } p = kT \left(\frac{\partial \ln Z}{\partial V} \right)_T,$$

$$\text{Entropy } S = k \left[\ln Z + T \left(\frac{\partial \ln Z}{\partial T} \right)_V \right], \quad (3.4)$$

$$\text{Enthalpy } H = kT \left[T \left(\frac{\partial \ln Z}{\partial T} \right)_V + V \left(\frac{\partial \ln Z}{\partial V} \right)_T \right],$$

where T is temperature and V is the volume of the molecular system. The various derivatives and expressions of the fundamental equations shown in 3.4 have an important physical significance. This paper introduces expressions that are important in terms of energy exchange processes. The various derivatives below also have a practical significance [4-9]:

$$\text{- Heat capacity at constant volume per mole: } C_v = \left(\frac{\partial U}{\partial T} \right)_V, \quad (3.5)$$

$$\text{- Heat capacity at constant pressure per mole: } C_p = \left(\frac{\partial H}{\partial T} \right)_p = C_v + \frac{TV\beta^2}{\chi}, \quad (3.6)$$

where M is the molecular mass.

The thermodynamic system consists of N particles associated by attractive forces. Atoms in a crystal lattice are not motionless, as they oscillate around their positions of equilibrium. At temperatures below the melting point, the motion of atoms is approximately harmonic [2,3]. This assembly of atoms has $3N-6$ vibrational degrees of freedom. The six vibrational degrees of freedom have been omitted and the number of vibrational degrees of freedom marked with $3N$.

Through the knowledge of independent harmonic oscillators, the distribution function Z [7] can be derived as follows:

$$Z = \left[\frac{\exp\left(-\frac{h\nu}{2k_B T}\right)}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)} \right]^{3N} \quad (3.7)$$

where ν is the oscillation frequency of the crystal. The term $h\nu/k$ is the Einstein temperature.

When comparing the experimental data for simple crystals, a relatively good match with the analytical calculations at higher temperatures is observed, whereas at lower temperatures the discrepancies are higher. This explains why Debye corrected Einstein's model by taking account of the interactions between a numbers of quantised oscillators. The Debye approximation treats a solid as an isotropic elastic substance. Using the canonical distribution, the partition function may be written as:

$$\ln Z = -\frac{9}{8} N \frac{\theta_D}{T} - 3N \cdot \ln\left(1 - \exp\left(-\frac{\theta_D}{T}\right)\right) + 3N \frac{T^3}{\theta_D^3} \int_0^{\theta_D/T} \frac{\xi^3}{\exp(\xi)-1} d\xi \quad (3.8)$$

In equation 3.8, θ_D is the Debye temperature. The following equation is obtained by expanding the third term in equation 3.8 into a series for a higher temperature range,

$$\frac{\xi^3}{\exp(\xi)-1} = \xi^2 - \frac{1}{2}\xi^3 + \frac{1}{12}\xi^4 - \frac{1}{720}\xi^6 + \dots \quad (3.9)$$

Using equations 3.8 and 3.9 leads to the following expression:

$$\ln Z = -\frac{9}{8} N \frac{\theta_D}{T} - 3N \cdot \ln\left(1 - \exp\left(-\frac{\theta_D}{T}\right)\right) + 3N \left(\frac{T}{\theta_D}\right)^3 \left[\begin{aligned} &\frac{1}{3}\left(\frac{\theta_D}{T}\right)^3 - \frac{1}{8}\left(\frac{\theta_D}{T}\right)^4 + \frac{1}{60}\left(\frac{\theta_D}{T}\right)^5 \\ &-\frac{1}{5040}\left(\frac{\theta_D}{T}\right)^7 + \frac{1}{272160}\left(\frac{\theta_D}{T}\right)^9 - \dots \end{aligned} \right] \quad (3.10)$$

The Debye characteristic temperature was determined by means of the Grüneisen independent constant γ :

$$\theta_D = CV^{-\gamma}, \quad (3.11)$$

where C is a constant, dependent on the material. This mathematical model can be used for the calculation of thermodynamic properties of polyatomic crystals. The derivations of the Einstein and Debye equations, outlined previously, apply specifically to monoatomic solids, namely those

belonging to the cubic system. However, experiments have shown that the Debye equation also predicts the values of specific heat and other thermophysical properties for certain other mono-atomic solids, such as zinc, which crystallises in the hexagonal system.

4 ANALYSIS AND RESULTS

The results below show a comparison of the analytical model obtained using the mathematical model shown in the sections above. Figure 4 shows the results for CuCl_2 , a comparison between the calculated results and the results obtained using the Shomate equation. In the previous results, the calculations of thermodynamic properties for solids are determined based on the following Shomate equation.

$$C_p = A + BT + CT^2 + DT^3 + \frac{E}{T^2}, \quad (4.1)$$

$$H = \int C_p dT, S = \int C_p \frac{dT}{T}. \quad (4.2)$$

Figure 5 shows the relative deviation for isobaric specific heat for Cu_2OCl_2 between the results obtained using the analytical model and the experimental results [12]. Figure 6 shows the results obtained using the mathematical model [6, 9] for isobaric specific heat of fluid and the Shomate equation. The results indicate a relatively good match between the mathematic model and the published results.

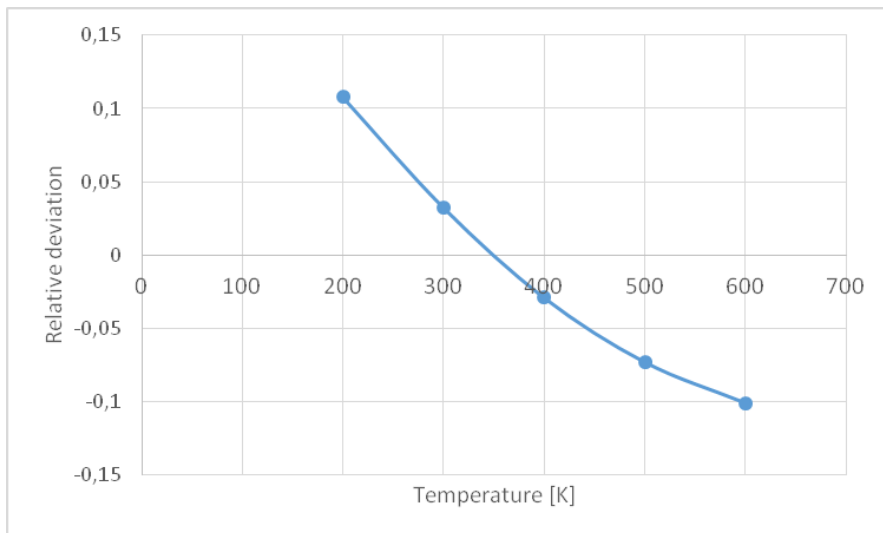


Figure 4: Relative deviation for isochoric specific heat for CuCl_2 between analytical data and the Shomate equation

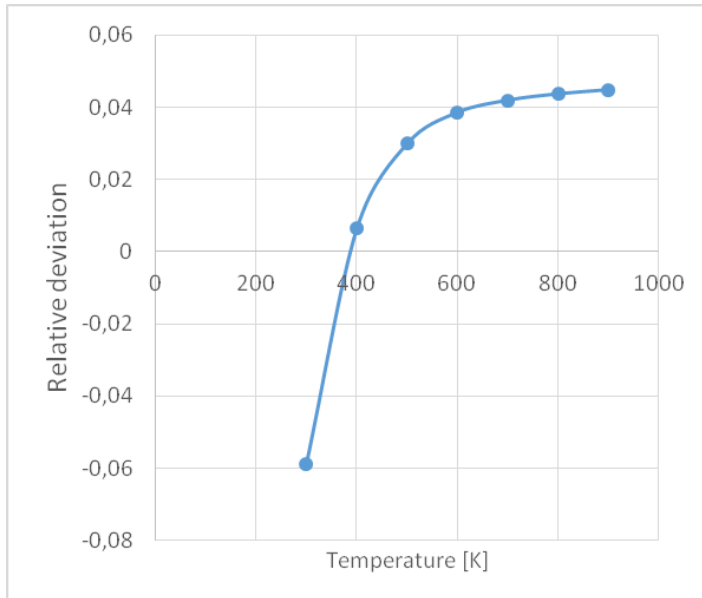


Figure 5: Relative deviation for isochoric specific heat between the analytical model and experimental results [14]

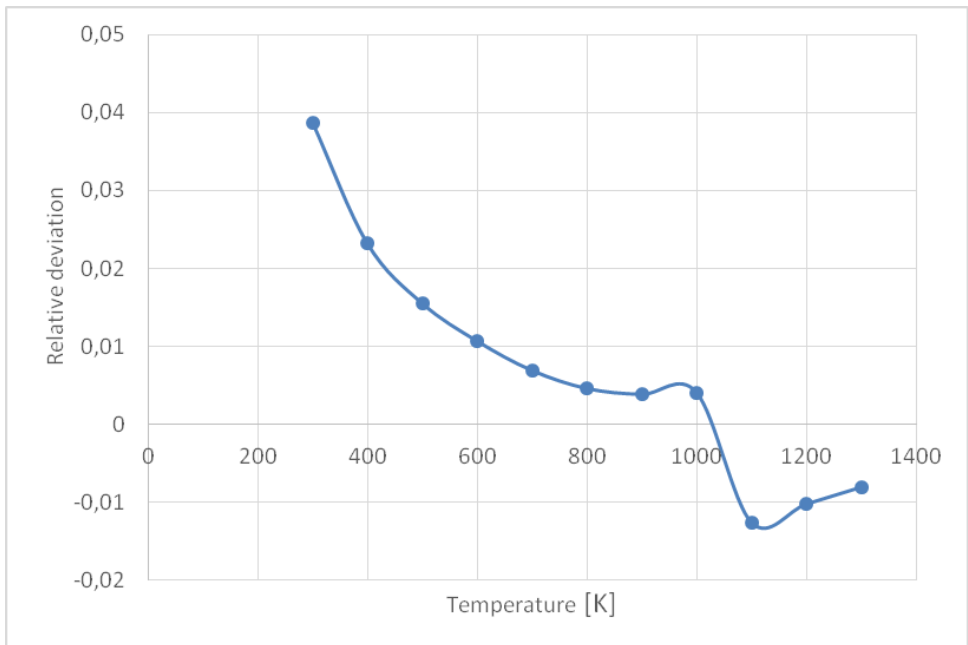


Figure 6: Relative deviation for isobaric specific specific heat for HCl between analytical data and the Shomate equation

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