

THE CALCULATION OF SPECIFIC HEATS FOR SOME IMPORTANT SOLID COMPONENTS IN HYDROGEN PRODUCTION PROCESS BASED ON CuCl CYCLE

by

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Hydrogen is one of the most promising energy sources of the future enabling direct production of power and heat in fuel cells, hydrogen engines or furnaces with hydrogen burners. One of the last remainder problems in hydrogen technology is how to produce a sufficient amount of cheap hydrogen. One of the best options is large scale thermochemical production of hydrogen in combination with nuclear power plant. copper-chlorine (CuCl) cycle is the most promissible thermochemical cycle to produce cheap hydrogen. This paper focuses on a CuCl cycle, and the describes the models how to calculate thermodynamic properties. Unfortunately, for many components in CuCl cycle the thermochemical functions of state have never been measured. This is the reason that we have tried to calculate some very important thermophysical properties. This paper discusses the mathematical model for computing the thermodynamic properties for pure substances and their mixtures such as CuCl, HCl, Cu₂OCl₂ important in CuCl hydrogen production in their fluid and solid phase with an aid of statistical thermodynamics. For the solid phase, we have developed the mathematical model for the calculation of thermodynamic properties for polyatomic crystals. In this way, we have used Debye functions and Einstein function for acoustical modes and optical modes of vibrations to take into account vibration of atoms. The influence of intermolecular energy we have solved on the basis of Murnaghan equation of state and statistical thermodynamics.

Key words: *hydrogen technology, thermochemical water splitting, hydrogen production, statistical thermodynamics, specific heats*

Introduction

Rather than deriving hydrogen from fossil fuels, a promising alternative is thermochemical decomposition of water. 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 24%. The production of hydrogen from electrolysis is very expensive. In contrast, thermo-chemical cycles to produce hydrogen promise heat-to-hydrogen efficiencies up to about 50%. This article examines the thermo-physical properties of a specific cycle called the copper-chlorine (CuCl) cycle, with particular relevance to nuclear-produced hydrogen. A detailed scheme regarding CuCl cycle is presented in literature [1, 2], and in tabs. 1 and 2.

In the CuCl cycle, water is decomposed into hydrogen and oxygen through intermediate CuCl compounds [1-4]. Nuclear-based “water splitting” requires an intermediate heat

exchanger between the nuclear reactor and hydrogen plant, which transfers heat from the reactor coolant to the thermo-chemical cycle. An intermediate loop prevents exposure to radiation from the reactor coolant in the hydrogen plant, as well as corrosive fluids in the thermo-chemical cycle entering the nuclear plant.

Table 1. 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]	36.4606	98.999	134.451	214	79.545

Table 2. Important chemical reactions in the CuCl process

Step	Reaction	Temperature range [°C]	Feed/Output (note: Q – thermal energy, V – electrical energy)
1	$2\text{Cu(s)} + 2\text{HCl(g)} \rightarrow \text{CuCl(l)} + \text{H}_2\text{(g)}$	430-475	Feed: Electrolytic Cu + dry HCl + Q Output: H ₂ + CuCl(l) salt
2	$2\text{CuCl(s)} \rightarrow 2\text{CuCl(aq)} \rightarrow \text{CuCl}_2\text{(aq)} + \text{Cu(s)}$	Ambient (electrolysis)	Feed: Powder/granular CuCl and HCl + V Output: Electrolytic Cu and slurry containing HCl and CuCl ₂
3	$\text{CuCl}_2\text{(aq)} \rightarrow \text{CuCl}_2\text{(s)}$	<100	Feed: Slurry containing HCl and CuCl ₂ + Q Output: Granular CuCl ₂ + H ₂ O/HCl vapours
4	$2\text{CuCl}_2\text{(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CuO} \times \text{CuCl}_2\text{(s)} + 2\text{HCl(g)}$	400	Feed: Powder/granular CuCl ₂ + H ₂ O(g) + Q Output: Powder/granular CuO × CuCl ₂ + 2HCl (g) Q ~ 117 kJ/mol H ₂
5	$\text{CuO} \times \text{CuCl}_2\text{(s)} \rightarrow 2\text{CuCl(l)} + 1/2\text{O}_2\text{(g)}$	500	Feed: Powder/granular CuO × CuCl ₂ (s) + Q Output: Molten CuCl salt + oxygen Q ~ 130 kJ/mol H ₂

The CuCl cycle is constructed as closed loop consisted from five steps [1, 2]. The mentioned five steps could we classify as HCl production step, oxygen production step, copper production step, drying step and hydrogen production step. For production of 1 kg of hydrogen in CuCl process we need 220 MJ of heat and 51.5 MJ of electricity. In the process are entering superheated stream, heat and small amount of electricity. The maximum temperature in the process is 550 °C, with new development of CuCl cycle we wish to reduce the maximum temperature approximately to 300 °C. In any case also present temperature is very interesting, which gives the CuCl cycle as one of the most perspective cycles for large hydrogen production in combination with nuclear power plant or coal power plant. One of the most important substances in the process is copper oxychloride (Cu₂OCl₂). The substance is classified as mineral melanothallite and for this substance is published limited number of experimental data with large discrepancies [1-8]. There is no critical point for this substance because copper oxychloride decomposes in a crystalline structure Cu₂OxCuCl₂. The temperature of decomposition varies regarding different literature between 352 °C and 400 °C [4]. Also this crystalline mixture is very important for CuCl cycle and enters oxygen production reactor where it is heated over 500 °C.

To calculate accurate the efficiency and other important parameters of CuCl cycle, we need exact values of thermodynamic properties for some components in CuCl cycle. In the presented article, we tried to calculate thermodynamic properties with help of statistical ther-

modynamics. It is possible to calculate thermodynamics properties with classical and statistical thermodynamics. In contrast to classical thermodynamics, statistical thermodynamics allows to develop mathematical models on the basis of molecular intramolecular and intermolecular energy of molecular system.

Statistical thermodynamics for solids

Classical thermodynamics calculates thermodynamic properties of matter on the basis of macroscopic observation of processes in the physical world. The calculation of thermodynamic properties of state is extremely important for industrial processes, such as processing plants, cooling plants, combustion processes, *etc.* There are many semi-empirical formulations (Van der Waals, Peng-Robinson, Redlich-Kwong, Soave, *etc.* [5]). Their advantage is mathematical simplicity. But equations are less accurate in the region of higher pressures. Numerous complex semi-empirical equations also exist for the calculation of thermodynamic properties of state (Benedict-Webb-Rubin – BWR, Lee-Kesler, Benedict-Webb-Rubin-Starling – BWRS and so on). The main drawback of semi-empirical equations is their limited use within only prescribed pressure and temperature limits. They also provide no direct insight into the microstructure of matter. Similarly, the calculation of the second virial coefficient, which takes into account the influence of the intermolecular potential on the interaction of molecules between the pairs of particles, does not provide sufficiently accurate forecasts when using semi-empirical equations. Most of these formulations can be derived theoretically, under the assumption of a rough influence of intermolecular attractive and repulsive forces.

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 [7-15]:

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

Define the partition function Z [5], 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 above assumptions, we can then write the canonical partition function for the one-component system in the following manner [9]:

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

The second term on the right-hand side of eq. (1) is called the configurational integral, f is the number of degrees of freedom of an individual molecule, $\vec{p}$ is momentum, $\vec{r}$ is the coordinate, and E_{vib} , E_{el} , E_{nuc} , and E_{pot} represent the vibrational energy, electron energy, nuclear energy of individual molecules and potential energy between two molecules, respectively.

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

$$Z = \frac{1}{\prod_i N_i! h^{N_i f_i}} \int \dots \int \exp\left(-\frac{E_{vib} + E_{el} + E_{nuc}}{k_B T}\right) d\vec{p}_1 d\vec{p}_2 \dots d\vec{p}_N \cdot \int \dots \int \exp\left(-\frac{E_{pot}}{k_B T}\right) d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N \quad (2)$$

In eq. (2) N_i is the number of molecules of the i -th component, and 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:

$$Z = Z_0 Z_{vib} Z_{el} Z_{nuc} Z_{conf} \quad (3)$$

For a system of many components, the partition function Z can be written as a product of partition functions for individual terms:

$$Z = \prod_i (Z_0 Z_{vib} Z_{el} Z_{nuc})_i Z_{conf} = \prod_i Z_i Z_{conf} \quad (4)$$

The partition function Z is a product of terms of the ground state (0), influence of electron excitation (el), influence of nuclei excitation (nuc) and the influence of the intermolecular potential energy (conf). In the presented mathematical model, we have neglected the influence of energy of electrons and influence of nuclear energy. Utilizing the canonical theory for computing the thermodynamic functions of the state leads to [5-10]:

$$\text{Pressure } p = kT \left(\frac{\partial \ln Z}{\partial T} \right)_V \quad (5)$$

$$\text{Internal energy } U = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V \quad (6)$$

$$\text{Free energy } A = -kT \ln Z \quad (7)$$

$$\text{Entropy: } S = k \left[\ln Z + T \left(\frac{\partial \ln Z}{\partial T} \right)_V \right] \quad (8)$$

$$\text{Free enthalpy, } G = -kT \left[\ln Z - V \left(\frac{\partial \ln Z}{\partial T} \right)_V \right] \quad (9)$$

$$\text{Enthalpy } H = kT \left[T \left(\frac{\partial \ln Z}{\partial T} \right)_V + V \left(\frac{\partial \ln Z}{\partial V} \right)_T \right] \quad (10)$$

where T is the temperature and V – the volume of the molecular system. The various derivatives and expressions of the fundamental eqs. (5)-(10) have an important physical significance. This paper presents expressions which are important with regards to energy exchange processes. The various derivatives below also have a practical significance:

$$\text{Coefficient of thermal expansion: } \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (11)$$

$$\text{Isothermal compressibility: } \chi = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (12)$$

$$\text{Heat capacity at constant volume per mole: } C_v = \left(\frac{\partial U}{\partial T} \right)_V \quad (13)$$

$$\text{Heat capacity at constant pressure per mole: } C_p = \left(\frac{\partial H}{\partial T} \right)_p = C_v + \frac{TV\beta^2}{\chi} \quad (14)$$

$$\text{Velocity of sound } c_0 = \sqrt{-V^2 \frac{1}{M} \left(\frac{\partial p}{\partial V} \right)_s} = \sqrt{-V^2 \frac{\frac{C_p}{T} \left(\frac{\partial T}{\partial V} \right)_p \frac{1}{M}}{\left(\frac{\partial V}{\partial T} \right)_p - \frac{C_p}{T} \left(\frac{\partial T}{\partial p} \right)_v}} \quad (15)$$

where M is the molecular mass.

Vibrational properties of solids

Our 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 [10-15]. This assembly of atoms has $3N-6$ vibrational degrees of freedom. We will neglect 6 vibrational degrees of freedom and mark the number of vibrational degrees of freedom with $3N$.

Through the knowledge of independent harmonic oscillators, the distribution function Z [5-11] can be derived as:

$$Z = \left[\frac{\exp\left(-\frac{h\nu}{2k_B T}\right)}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)} \right]^{3N} \quad (16)$$

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

When comparing the experimental data for simple crystals, a relatively good match with 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 number of quantized oscillators. The Debye approximation treats a solid as an isotropic elastic substance. Using the canonical distribution, the partition function may be written as:

$$\ln Z = -\frac{9}{8} N \frac{\theta_D}{T} - 3N \ln \left(1 - \exp\left(-\frac{\theta_D}{T}\right) \right) + 3N \frac{T^3}{\theta_D^3} \int_0^{\theta_D/T} \frac{\zeta^3}{\exp(\zeta) - 1} d\zeta \quad (17)$$

In eq. (17), θ_D is the Debye temperature. By expanding the third term in eq. (17) into a series for a higher temperature range:

$$\frac{\zeta^3}{\exp(\zeta) - 1} = \zeta^2 - \frac{1}{2}\zeta^3 + \frac{1}{12}\zeta^4 - \frac{1}{720}\zeta^6 + \dots \quad (18)$$

Using eq. (17) and eq. (18) leads to the following expression:

$$\ln Z = -\frac{9}{8}N\frac{\theta_D}{T} - 3N \ln \left(1 - \exp \left(-\frac{\theta_D}{T} \right) \right) + 3N \left(\frac{T}{\theta_D} \right)^3 \left[\frac{1}{3} \left(\frac{\theta_D}{T} \right)^3 - \frac{1}{8} \left(\frac{\theta_D}{T} \right)^4 + \frac{1}{60} \left(\frac{\theta_D}{T} \right)^5 - \right. \\ \left. - \frac{1}{5040} \left(\frac{\theta_D}{T} \right)^7 + \frac{1}{272160} \left(\frac{\theta_D}{T} \right)^9 - \dots \right] \quad (19)$$

The relation between the Einstein and Debye temperature may be written as $\theta_E = 0.735 \cdot \theta_D$.

The Debye characteristic temperature was determined by means of the Gruneisen independent constant [12-15], γ :

$$\theta_D = CV^{-\gamma} \quad (20)$$

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 monoatomic solids, such as zinc, which crystallizes in the hexagonal system.

Consider that the crystal contains N molecules, each composed of s atoms [10-14]. Since there are Ns atoms, the crystal as a whole has $3Ns$ vibrational modes. A reasonable approximation is obtained by classifying the vibrations as follows:

- $3N$ lattice vibrations, which are the normal modes in the Debye model (acoustical modes), and
- independent vibrations of individual molecules, in which bond angles and lengths may vary (there must be $3n(s-1)$ of these optical modes, which were expressed by the Einstein model).

Murnaghan equation of state for solids-influence of intermolecular potential energy

The internal energy of a solid, u_T can be expressed as the sum of the following two terms:

$$u_T(v, T) = u_0(v) + u_D(T, v) \quad (21)$$

where u_0 represents the cohesive energy at zero temperature. On the basis of relations from classical thermodynamics, $(-p = (\partial u / \partial v)_s)$,

$$p = p_0 + u_D(\gamma / V) \quad (22)$$

Using constants explained in [2], the pressure at zero temperature p_0 can be expressed by:

$$p_0 = B_0 \frac{3 \left[\sqrt[3]{\frac{V}{V_0}} - 1 \right]}{\sqrt[3]{\left(\frac{V}{V_0} \right)^2}} e^{-\alpha} (1 - 0.15\alpha + 0.05\alpha^2) \quad (23)$$

In the eq. (23) B_0 and α are parameters, defined and explained in the literature [10-15].

Results and discussion

In this section, results of the thermodynamic property evaluations will be performed over a range of temperatures. In fig. 1, the predicted enthalpy of CuCl in the liquid and gas regions is shown. A step change is observed at the phase transition point. Additional results of entropy at varying temperatures are shown in fig. 2. In the previous results, the calculations of thermodynamic properties for solids are determined based on the following Shomate equation.

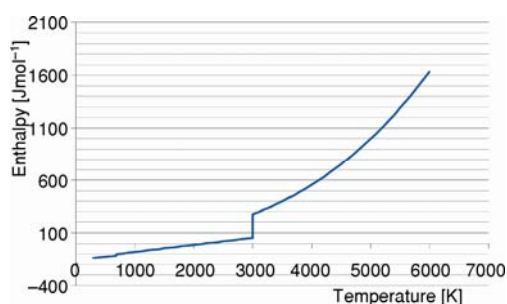


Figure 1. Enthalpy of CuCl in the solid-liquid-gas region (based on Shomate's equation)

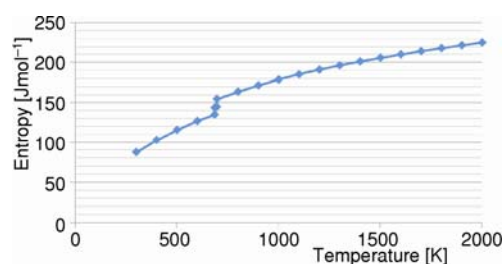


Figure 2. Entropy of CuCl in the solid-liquid-gas region (based on Shomate's equation)

$$C_p = A + BT + CT^2 + DT^3 + \frac{E}{T^2} \quad (24)$$

$$H = \int C_p dT, S = \int C_p \frac{dT}{T} \quad (25)$$

Past studies [5, 14-17] have shown that CuCl exists in two crystalline forms, namely a cubic form up to 412 °C and a beta-hexagonal form above this temperature. The melting point of CuCl is 423 °C, so the temperature range of the beta-hexagonal form is small. CuCl may have one of the following three preferred forms at any given temperature: CuCl (liquid), CuCl (SC) (cubic) and CuCl (SB) (beta-hexagonal).

Figures 3 and 4 show the temperature variation of specific heats, obtained by statistical thermodynamics, for some important components (copper oxychloride Cu_2OCl_2 and cupric oxide CuO) in CuCl hydrogen production cycle. The analytical results we have compared experimental data obtained in scientific literature [7]. Our model shows good agreement with experimental data.

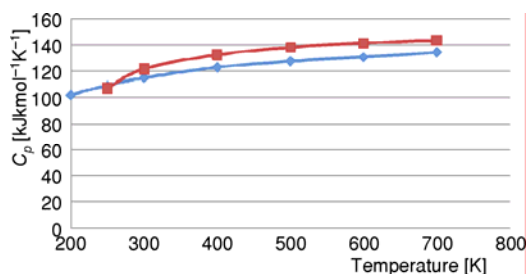


Figure 3. Specific heats for Cu_2OCl_2 in comparison between analytical calculation by statistical thermodynamics (upper) and model on the basis of experimental data (lower)

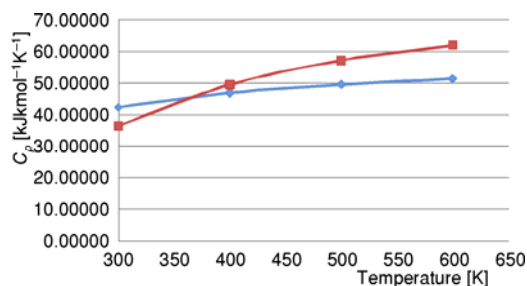


Figure 4. Specific heats for CuO in comparison between analytical calculation by statistical thermodynamics (upper) and model on the basis of experimental data (lower)

Conclusion

The copper-chlorine thermo-chemical hydrogen production cycle is one of the possible solutions for large scale hydrogen production. The presented article shows the developed mathematical model for calculation of thermo-physical properties. The model allows calculating thermodynamic properties for some components cooperating in CuCl hydrogen production cycle. The model is developed on the basis of statistical thermodynamics, where we have taken into accounts vibrations of atoms and influence of intermolecular potential. The comparison between analytical calculation and the model on the basis of experimental data shows good agreement.

Nomenclature

A	– free energy, [J]
c_{0S}	– isentropic velocity of sound, [ms^{-1}]
c_{0T}	– isothermal velocity of sound, [ms^{-1}]
C_v	– heat capacity at constant volume per mole, [$\text{Jkmol}^{-1}\text{K}^{-1}$]
C_p	– heat capacity at constant pressure per mole, [$\text{Jkmol}^{-1}\text{K}^{-1}$]
CuCl	– copper-chlorine thermochemical process, [–]
E	– energy, [J]
E_S	– isentropic elastic module, [Nmm^{-2}]
E_T	– isothermal elastic module, [Nmm^{-2}]
f	– number of degree of freedom, [–]
H	– enthalpy, [Jkmol^{-1}]
k_B	– Boltzmann constant, [JK^{-1}]
m	– mass, [kg]
N	– number of molecules in system, [–]
p	– momentum, pressure, [kgms^{-1} , Pa]
r_{ij}	– intermolecular distance, [m]
s	– number of atoms in molecule, [–]
S	– entropy, [$\text{Jkmol}^{-1}\text{K}^{-1}$]

T	– temperature, [K]
V	– volume, [m^3]
Z	– partition function, [–]

Greek symbols

β	– volumetric expansion coefficient, [K^{-1}]
γ	– Grüneisen constant, [–]
θ	– characteristic temperature, [K]
θ_D	– Debye temperature, [K]
θ_E	– Einstein temperature, [K]
ν	– oscillation frequency, [s^{-1}]
χ_S	– isentropic compressibility, [bar^{-1}]
χ_T	– isothermal compressibility, [bar^{-1}]

Superscripts and subscripts

0	– ground state
conf	– configuration
el	– influence of electron excitation
nuc	– influence of nuclear excitation
pot	– potential energy
vib	– vibration

References

- [1] Naterer, G. F., *et al.*, Clean Hydrogen Production with the Cu-Cl Cycle – Progress of International Consortium, Part 2, Simulations, Thermochemical Data and Materials, *Int. J. Hydrogen Energy*, 36 (2011), 24, pp. 15486-15501

- [2] Wang, Z. L., Naterer, G. F., Greenhouse Gas Reduction in Oil Sands Upgrading and Extraction Operations with Thermochemical Hydrogen Production, *Int. J. Hydrogen Energy*, 36 (2011), 24, pp. 15486-15501
- [3] Okabe, H., *et al.*, New Pyrochlore-like Compound Cu_2OCl_2 with $S=1/2$, *Journal of Physical Society of Japan*, 75 (2006), 123765, pp. 1-4
- [4] Nixon A., *et al.*, Thermochemical Production of Hydrogen Synthesis, Characterization, and Decomposition of Copper Oxychloride, *J. Therm. Analys. Calorim.*, 110 (2011), 3, pp. 1095-1105
- [5] Krivoichiev, S. V., *et al.*, The Cuprite-Like Framework of OCu_4 Tetrahedra in the Crystal Structure of Synthetic Melanothallite Cu_2OCl_4 and its Negative Thermal Expansion, *The Canadian Mineralogist*, 40 (2002), pp. 1185-1190
- [6] Zamfirescu, C., *et al.*, Thermophysical Properties of Copper Compounds in Copper-Chlorine Thermochemical Water Splitting Cycles, *International Journal of Hydrogen Energy*, 35 (2010), 10, pp. 4839-4852
- [7] Parry T., Thermodynamics and Magnetism of Cu_2OCl_2 , M. Sc. thesis, Birgham Young University, Provo, Ut., USA, 2008
- [8] Kawashima, K., *et al.*, Antiferromagnetic Ordering in Cu_2OCl_2 Studied by the Muon Spin Rotation/relaxation Technique, *Journal of Physics (condens. Matter)*, 19 (2007), pp. 1-5
- [9] Lewis, M. A., *et al.*, Evaluation of Alternative Thermochemical Cycles, Part I, The Methodology, *International Journal of Hydrogen Energy*, 34 (2009), 9, pp. 4115-4124
- [10] Avsec, J., Naterer, G. F., Thermodynamic Property Evaluation of Copper-Chlorine Fluid Components at High Temperatures, AIAA 40th Thermophysics conference, Seattle, Wash., USA, 2008
- [11] McClelland, B. J., *Statistical Thermodynamics*, Chapman and Hall, London, 1980
- [12] Munster, A., *Statistical Thermodynamics*, Springer-Verlag, Berlin, Germany, 1974
- [13] Avsec, J., Watanabe, K., An Approach to Calculate Thermodynamic Properties of Mixtures Including Propane, n-Butane and Isobutane. *Int. J. Thermophys.*, 26 (2005), 6, pp. 1769-1780
- [14] Avsec, J., Oblak, M., Thermal Vibrational Analysis for Simply Supported Beam and Clamped Beam, *J. Sound Vib.*, 308 (2007), 3/5, pp. 514-525
- [15] Avsec, J., Marčič, M., Calculation of Elastic Modulus and Other Thermophysical Properties for Molecular Crystals, *J. thermophys. heat transf.*, 16 (2002), 3, pp. 463-468
- [16] Rosen, M. A., *et al.*, Nuclear-Based Hydrogen Production with a Thermochemical Copper-Chlorine Cycle and Supercritical Water Reactor, Canadian Hydrogen Association Workshop, Montreal, Quebec, Canada, 2006
- [17] Mathias, P. M., Modeling of the Copper Chloride Thermochemical Cycle: Thermodynamic Properties of CuCl , Technical Report, Argonne National Laboratory, DuPage County, Ill., USA, 2006