Modeling of Metallurgical Slag Features

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1

INTRODUCTION

In Mendeleev's periodic table there are 118 chemical elements [1] belonging to metals, semi-metals and non-metals. They constitute a countable group of substances with various, mostly known properties. However, when we start to combine them, we get a countless group of various compounds belonging to alloys, organic and inorganic compounds, polymers, composites and others, with various physicochemical, mechanical and technological properties. Even popular metals with a very high purity class, the so-called ultra-high purity metals, are not fully understood and may have surprising properties, different from those commonly recognized in a lower purity class [2, 3].

Determining the properties of materials is the essence of all research and the basis for their use in industry. They bring wide-ranging and new opportunities that are associated with them, new perspectives, but also possible threats that may result from poorly understood characteristics [4].

The search for new materials for use in industry, without knowing their properties, is a very difficult issue. Over the centuries, some materials and their properties were discovered accidentally [5]. Others were the result of long and painstaking experiments. However, each time a newly discovered material has to be tested for its suitability, which is a long, expensive process and does not guarantee satisfactory results. However, you should look for methods and tips that can be applied in a certain direction. Digital tools, modelling of physicochemical properties and simulations can be helpful in this task [6]. Thanks to properly created data processing algorithms, it is possible to determine new properties with high accuracy and probability and modern materials that have not yet been produced and tested. Materials that, through experimental calculations, can demonstrate the sought-after properties that will guarantee the expected results. Such materials can finally be produced and tested by empirical methods that confirm the achievement of the assumed properties, bypassing the long period of expensive research, which does not guarantee full success.

It should also be noted that the vast majority of substances from which products or semi-finished products are made come from the natural environment, and the source of which may be the geo-, litho- or even the biosphere. Many minerals, compounds or minerals are processed in industrial plants or laboratories to obtain a desired product, which is often a substrate in the production of another material.

Elements or their compounds, being the input or output product of a given technological process, are not characterized solely by physical or chemical properties. Their mechanical, technological or other properties characteristic for a given group of materials are also very important. One of such groups are metallurgical slags, which perform very important functions in pyrometallurgical processes. They allow not only to shield the liquid metal from the harmful effects of the atmosphere, but also to protect the furnace lining, to retain reaction products inside the metal bath, and most importantly, to remove impurities from liquid metal to the slag phase [7].

The aim of the work is to collect and systematize information on the determination of refining properties of metallurgical slags. In addition, the author will attempt to determine a mathematical and physical model using digital tools to determine the refining properties of extraction coatings.

2

PHYSICAL PROPERTIES OF SLAGS

Physical properties are a characteristic set of quantitatively measurable or qualitatively descriptive information that defines any material substance. In the case of slags, they describe the key features that will have a significant impact on the final effect from the point of view of pyrometallurgical processes. Basic physical properties include melting point, density, viscosity and wettability with regard to non-metallic inclusions and electrical and thermal conductivity.

2.1 Melting point of slags, metals and alloys

This is the basic physical parameter defining the state in which the slag mixture starts to dissolve and goes from solid to liquid state. However, it should be remembered that in the case of slag mixtures there is a concept of liquidus and solidus temperature, i.e. a state between which some components have already dissolved and others remain in a solid state. However, due to the nature of the mixture contained in slags, their melting point is often lower than that of individual components considered individually. As a result of the contact of the grains of the mixture, a diffusion connection occurs between them, which leads to the melting of the layer of grains and coalescence of particles, which ultimately leads to complete melting of the system [16, 17, 18, 19].

Thus, the melting point dominates all other physical and chemical properties that directly affect it. In ternary systems, both the melting point and other physical properties can be represented by the so-called the Gibbs system [20, 21], which presents the properties of the system written on the plan of a triangle (Fig. 2.1.1). The corners of the triangle indicate the specific component of the mixture, the sides describe the mixture consisting of two components in certain proportions, and the inside of the triangle refers to the combination of three components with percentage proportions determined by the position of the point inside the figure. The figure below shows a typical Al_2O_3 – CaO – SiO_2 system with marked values defining the melting point of the system [22]. In the case of systems consisting of

more elements, the graphical representation is not so easy to implement, then the most reasonable method of description seems to be a tabular representation of the data.

In pyrometallurgical processes, the aim is to ensure that the melting point of the slag is really low, thanks to which the costs of liquefaction of the components can be reduced. The melting point value itself can be measured with any type of thermocouple, but it is necessary to be able to recognize discrepancies in the data resulting from the test method and discrepancy data by different authors.

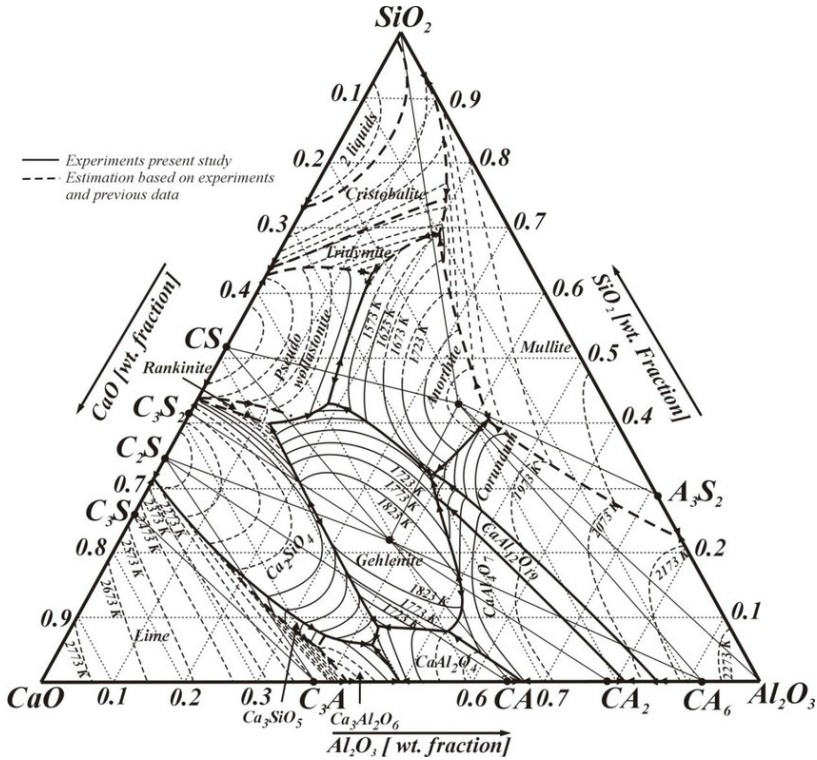

Fig. 2.1.1. Representation of the melting point of a 3-component system on the Gibbs triangle [23]

Determination of the melting point (solidus/liquidus), i.e. the nucleation and crystallization temperature, especially in the case of slags, are very difficult tasks. Such tests can be performed on the thermal analyser

TG+DTA. However, when studying the nucleation of small thermal effects, they appear as a small and diffuse exothermic peak on the DTA curve. On the other hand, the preceding peak corresponds to the crystallization process. Attention should also be paid to the exothermic effects of DTA measuring devices, which should be properly calibrated. The sensitivity and measurement of DTA should be high, and the heating frequency should be fast. The presence of two endothermic peaks on the DTA curve makes it possible to take into account the influence of the solidus temperature (eutectic melting point) and the liquidus temperature (melting point of the excess phase), which is used in studies [24].

From the point of view of considerations, the model presented by the author [6] seems interesting, as it shows a close relationship between the melting point and the density of substance. It is defined by the relationship:

$$T_{top} = \frac{\rho_n}{\left(\frac{1}{l_{top} + r}\right)^3 \cdot \frac{M \cdot \beta}{N_A}} + 273.15 - \left(\frac{1}{\beta}\right) \quad (1)$$

where:

T_{top} – melting point
ρ_n – density under normal conditions
l_{top} – the distance between the atoms of matter at the melting point
r – atomic radius
M – molar mass
β – coefficient of volumetric expansion
N_A – Avogadro's number

In the proposed formula, the l_{top} element will refer to the distance between atoms at the melting point and can be described by the relationship:

$$l_{top} = \frac{1 - (n_l \cdot r)}{n_l} \quad (2)$$

where:

n_l – This is the theoretical number of atoms in the crystal lattice of the metal in the linear direction. This value can be determined based on the number of atoms in the volume described by the density of the material at the melting point. You can save it as:

$$n_l = \left(\frac{V \cdot \rho_n \cdot N_A \cdot M}{(\Delta T \cdot \beta) + 1}\right)^{\frac{1}{3}} \quad (3)$$

where:

V – the volume of the material, in this case 1 m^3
ΔT – the difference between the melting point of the material and the temperature under normal conditions, i.e. 273.15 K.

Based on the research conducted by the author, it can be concluded that the proposed relationship is true for a large group of elements. The mean absolute error between the calculated value and the actual value is very small, only 0.25 K in one case and much less in the others.

The table (Tab. 2.1.1) below shows a comparison of the melting point calculated using the presented model with the temperature determined on the basis of experimental studies.

Tab. 2.1.1. Comparison of the melting point value calculated from the formula with the values determined experimentally.

Chemical element symbol	Calculation melting point (K)	Melting point determined experimentally (K)	Absolute error (K)
Li	453.4395081	453.6900000	0.2504919
Be	1560.0000000	1560.0000000	0.0000000
Na	370.8700000	370.8700000	0.0000000
Mg	923.0000000	923.0000000	0.0000000
Al	933.4700000	933.4700000	0.0000000
Si	1687.0000000	1687.0000000	0.0000000
K	336.5300000	336.5300000	0.0000000
Ca	1115.0000000	1115.0000000	0.0000000
Sc	1814.0000000	1814.0000000	0.0000000
Ti	1941.0000000	1941.0000000	0.0000000
V	2183.0000000	2183.0000000	0.0000000
Cr	2180.0000000	2180.0000000	0.0000000
Mn	1519.0000000	1519.0000000	0.0000000
Fe	1811.0000000	1811.0000000	0.0000000
Ni	1728.0000000	1728.0000000	0.0000000
Co	1768.0000000	1768.0000000	0.0000000
Cu	1357.7700000	1357.7700000	0.0000000

Zn	692.6800000	692.6800000	0.0000000
Ge	1211.4000000	1211.4000000	0.0000000
Sr	1050.0000000	1050.0000000	0.0000000
Y	1799.0000000	1799.0000000	0.0000000
Zr	2127.3000000	2127.3000000	0.0000000
Nb	2750.0000000	2750.0000000	0.0000000
Mo	2896.0000000	2896.0000000	0.0000000
Ru	2607.0000000	2607.0000000	0.0000000
Rh	2237.0000000	2237.0000000	0.0000000
Pd	1828.0500000	1828.0500000	0.0000000
Ag	1234.9300000	1234.9300000	0.0000000
Cd	594.2200000	594.2200000	0.0000000
In	429.7500000	429.7500000	0.0000000
Sn	505.0800000	505.0800000	0.0000000
Sb	903.7800000	903.7800000	0.0000000
Te	722.6600000	722.6600000	0.0000000
Ba	1000.0000000	1000.0000000	0.0000000
Hf	2506.0000000	2506.0000000	0.0000000
Ta	3290.0000000	3290.0000000	0.0000000
W	3695.0000000	3695.0000000	0.0000000
Re	3459.0000000	3459.0000000	0.0000000
Os	3306.0000000	3306.0000000	0.0000000
Ir	2739.0000000	2739.0000000	0.0000000
Pt	2042.0000000	2042.0000000	0.0000000
Au	1337.3300000	1337.3300000	0.0000000
Tl	577.0000000	577.0000000	0.0000000
Pb	600.6100000	600.6100000	0.0000000
Bi	544.4000000	544.4000000	0.0000000

In order to be able to determine the melting point (solidus/liquidus) of materials occurring in pyrometallurgical processes, a special laboratory stand was built [25] (Fig. 2.1.2). The designed laboratory stand has been constructed in such a way that it is possible to conduct research not only in the laboratory, but, if necessary, it can be easily transported to the production plant in order to perform appropriate measurements. The stand allows for a simple thermal analysis, i.e. a method of heating curves, which boils down to continuous and dynamic testing of the temperature of a sample heated or cooled at a constant speed. Thanks to the conducted tests, heating/cooling curves of a given sample are obtained, showing the value of temperature as a function of time. The basic possibilities offered by the built system are the

study of melting and crystallization processes of metals and alloys and slags, the ability to draw phase equilibrium diagrams of the tested substances, as well as the ability to determine the degree of purity of a substance thanks to the knowledge of its melting points.

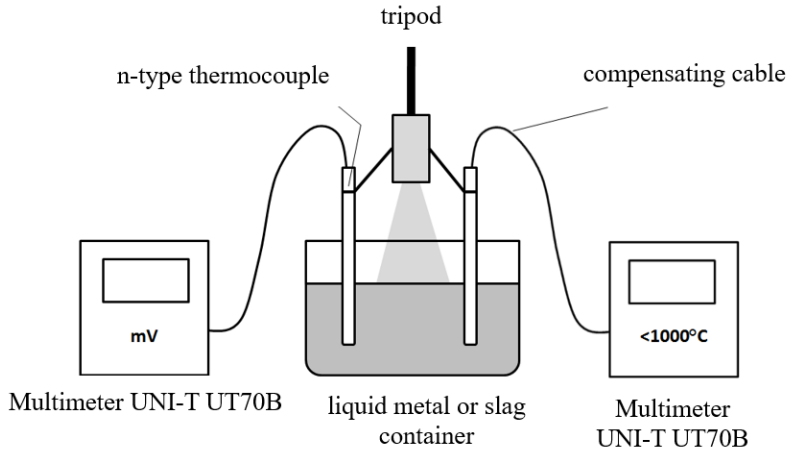

Fig. 2.1.2 Laboratory stand for testing the melting point of materials.

The working elements of the system are N-type thermocouples with a 300 mm long probe and a 100 cm long compensating cable for connecting them to the appropriate meter. According to their manufacturer, they are made of a nicrosil alloy and allow temperature measurement in the range from -230^0 C to +1300 °C. It is worth paying attention to the crucible itself with the test sample, which was cast from steel, and the walls are 1 cm thick at the narrowest point. Thanks to this design, the sample can not only be safely placed in the vessel, but also melted in the laboratory furnace, without fear of damaging the vessel itself. In addition, the process of cooling the material in this case lasts much longer, thanks to which it is possible to record thermal transformations taking place in the system more accurately. thermocouples are connected to UNI-T UT70B multimeters. The system here uses 2 different measurements to eliminate the measurement error of the test sample. The first of the multimeters directly measures the temperature read by the probe. The second probe is in turn connected to the second meter. The Seebeck effect was used here, which is a thermoelectric phenomenon involving the generation of an electromotive force in a circuit whose two metal ends have different temperatures. In this case, a direct measurement of the voltage expressed in mV takes place. The measurement

with this method can be carried out in the entire measuring range of the thermocouple, i.e. up to the temperature of 1300 °C. In order to convert the voltage value into temperature, the thermocouple can be scaled in an electric furnace by examining its behaviour in relation to the reference element.

In addition, the GM 900 pyrometer was added to the system, with the help of which it is possible to read the temperature of the upper layer of liquid slag and the reactions taking place on its surface after removal from the furnace, which, from the point of view of the liquid metal-slag-atmosphere system, are the most intense here.

The laboratory stand fulfils its tasks very well, as evidenced by numerous tests carried out with its use, e.g. for determination of solidus and liquidus temperatures of liquid metals and alloys [25, 26], as well as for determination of entire phase equilibrium diagrams [27].

For example, below (Fig. 2.1.3) the solidification characteristics of converter slags at the described station are presented. According to research, the dominant oxides in this type of systems are calcium oxides CaO (approx. 35-38%) and iron oxides (approx. 26-33%). Silicon oxides (approx. 10-15%), magnesium oxides MgO (approx. 7-8%), aluminium oxides (approx. 2-5%) and manganese oxides (approx. 2-5%) have a smaller share. 4%). You can also find small amounts of phosphorus oxides P_2O_5 (approx. 1-2%). The amounts of other oxides (e.g. sodium, titanium, potassium) are below 1% [28]. According to the literature, the melting point of this type of slag ranges from 1000 to 1100 °C [29].

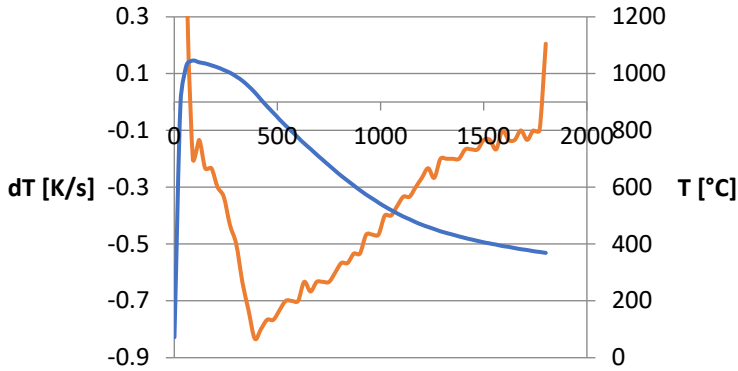

Fig. 2.1.3 Solidification characteristics of converter slag.

Based on the analyses carried out, the solidus temperature of the system is 934 °C (point P2), and the liquidus temperature is 1046 °C (point P1). However, it should be remembered that the thermocouples immersed in the liquid charge have copper, thermal covers with a diameter of 6 mm and a wall thickness of 1 mm. Based on the tests carried out, which allowed the calibration of the readings of the measuring station [26], the reading of each value should be increased by 62.5 °C. So, in our case, the solidus temperature of the system is 996.5 °C, and the liquidus temperature is 1108.5 °C.

2.2 Slag density

According to the definition, density is understood as specific mass, i.e. the ratio of body mass to the volume they occupy at a specific temperature [30]. According to this definition, the higher the temperature, the greater the volume of the substance, and thus its density, so the specific mass will decrease. In order to better define the properties of substances, several concepts of density have been introduced. Density understood as specific mass does not take into account the presence of pores in the volume of the material. Theoretical density (so-called roentgenographic) is determined on the basis of the dimensions of an elementary cell of matter determined by X-ray diffraction and the amount of and the type of atoms that make up that cell. Finally, the bulk density (the so-called apparent density) takes into account the presence of pores in the volume of the sample. Hence the specific density of quartzite in the form of sand is 2.72 g/cm^3, and the bulk density is 1.55-1.65 g/cm^3. In turn, the specific and bulk density of structural steel is the same and amounts to 7.85 g/cm^3 [31]. In the context of metallurgical slags, the term bulk density can also be found. The term obviously refers to bulk materials and will describe the ratio of the weight of the uncompressed dry matter of a given fraction to the volume of the container that this fraction fills.

In connection with the above, it should be borne in mind that the presence of pores in materials can significantly affect the physicochemical properties of materials. The proof of this can be a simple test carried out by the author on powdered aluminium. Well, aluminium powder placed in a furnace on a ceramic pad at 800 °C does not melt into liquid metal. Meanwhile, a compact formed from the same powder under a pressure of 15 MPa and placed in the same furnace conditions as the first compact melts into liquid metal.

In the case of the specific gravity of a substance, it can be regarded to some extent as the equivalent of density. However, in this case, the specific gravity is the ratio of the density of the substance to another known (so-called standard) density, which is most often water, whose specific gravity is about 1 g/cm^3 [1].

It should be noted that the nature of slag mixtures, which allows the use of their refining and protective properties, results from the fact that their specific gravity is much lower than the specific gravity of molten metal. Slag can remain on the surface of the metallic bath, and non-metallic inclusions can move towards it. In general, it can be assumed that ceramic materials have a lower density than metallic materials, although exceptions can be found, e.g. related to aluminium or titanium and their alloys [31]. It is also worth noting that the specific gravity of molten slag is about 2.6 g/cm3, while the specific gravity of molten metal, e.g. copper, in the temperature range of 1100-1400 °C is in the range of 7.65 – 8.00 g/cm^3 [32]. Hence the durability of the two separate phases in pyrometallurgical processes it is quite stable.

It is worth noting, however, that the low bulk density of slag, due to the presence of pores in its volume, may cause difficulties with the possibility of melting the sample. In addition, the introduction of carbon or carbide into the system during refining processes may not bring the full expected effects. These compounds have a very low density compared to the density of the refining coating, hence they will not want to enter it, but only stay on its surface. They will strongly react especially with the melting atmosphere, affecting non-metallic inclusions in the liquid metal to a small extent.

In the context of density determination, the theoretical model of density determination presented earlier by the author is interesting [6, 33]. This describes the dependency:

$$\rho_{STP} = \left(\frac{Az^7+Bz^6+Cz^5+Dz^4+Ez^3+Fz^2+Gz+H}{r_{at}}\right)^3 \cdot m_A \qquad (4)$$

where:
ρ_{stp} – the density of the substance under normal conditions (STP – Standard Conditions for Temperature and Pressure – temperature: 0 °C, pressure: 1000 hPa)
A, B, C, … – polynomial coefficients were determined experimentally and correspond to the course of the polynomial function, the degree of function

and the coefficients themselves are strictly defined in relation to a given period of the periodic table of elements
z – atomic number
r_{at} – atom radius (empirical value)
m_A – absolute atomic mass

The above formula was developed on the basis of information about the atomic structure of matter. Since density is defined as the ratio of a substance's mass to its volume, one may be tempted to make a simple reference to the atomic structure of the elements. The mass of a substance can be described by information about the absolute atomic mass, which is expressed in the unit u. This unit corresponds to a fraction of a kilogram and is equal to $1{,}66054 \cdot 10^{-24}$ grams. To determine the density of a substance, you also need information about the number of atoms in a given volume, which can be determined using Avogadro's number. It should also be remembered that the diameter of the atom is important, a certain number of which will occupy a certain space. Knowing their number, it will also be possible to determine the theoretical distance between atoms in a crystal lattice of a given volume. The above concept works perfectly well for all elements from groups II, III and VII of the periodic table. The calculated density value is obtained with a very high accuracy and an error of less than 0.00005%. For elements from groups IV, V and VI, the calculated accuracy was slightly lower, but still satisfactory. 75% of the analysed elements had a calculation error of less than 6%. Only for 14 elements, the discrepancies in the results of calculations related to the experimental values from the chemical tables were slightly larger and ranged from 7 to 39%. It is also worth noting that when determining the density of elements from groups IV, V and VII of the periodic table, the presented formula required the use of a 7th order polynomial, which guaranteed obtaining acceptable results. In addition, it should be noted that the complexity of the polynomial depends on the degree of the period of the analysed root, and the value of the coefficients is very large and reaches 22 decimal places. An attempt to reduce the number of seats had a very negative impact on the results and increased the value of the calculation error. Therefore, it was necessary to leave such high accuracy. As you can easily guess, the calculations required the use of appropriate digital tools and spreadsheets. Without their help, conducting such thorough analysis would be much more difficult. The table below (Tab. 2.2.1) presents the values of the polynomial relating to dependence no. 4.

Tablica. 2.2.1. Determining the value of the polynomial in dependence no. 4.

Period number	Polynomial coefficient number			
	7	6	5	4
II	0	0	0	0
III	0	0	$-4.9189239166666 5*10^{-4}$	0.03505997175
IV	$3.82563839391743*10^{-8}$	$-6.16424670551513*10^{-6}$	0.000422142170896459	-0.015907030024395
V	0	$1.34172286909084*10^{-6}$	-0.000352019045373507	0.038367454559976
VI	0	$-2.31787597226639*10^{-8}$	$9.71940359429707*10^{-6}$	-0.0016920993969052
VII	0	0	$-7.37956290277771*10^{-4}$	0.33726334890277
Period number	Polynomial coefficient number			
	3	2	1	Free expression
II	0.011919791	-0.1862270005	0.8642958585	-0.717544527
III	-0.98595032954166	13.68042430375	-93.7422457685665	254.568778866997
IV	0.35501400368175	-4.66450647828032	33.09122555702	-95.807156089588
V	-2.22377495488247	72.2930050018278	-1249.89223615025	8979.39412093296
VI	0.15655783363704 6	-8.11942707717231	223.803181139243	-2560.94730829028
VI	-61.6482869037425	5633.722164140 25	-257389.906797486	4703253.57396151

On the basis of such a model, it was possible to perform calculations for various substances present in the periodic table. The following tables (tab. 2.2.2 – 2.2.7) show the calculated value of density, comparing it with the value determined experimentally. For easier interpretation of the results, the calculation error value is also given in the last column.

Tablica 2.2.2. Comparison of empirical and calculated values from pattern no 4 - Period II

Calculation result	Experimental density	The name of the chemical element	Error [%]
535000.0003	535000.0000	**Lit**	0.00000
1848000	1848000.000	**Beryllium**	0.00000
2460000.005	2460000.000	**Boron**	0.00000
2260000.004	2260000.000	**Carbon**	0.00000

Tablica 2.2.3. Comparison of empirical and calculated values from pattern no 4 - Period III

Calculation result	Experimental density	The name of the chemical element	Error [%]
968000.0027	968000.000	**Sodium**	0.00000
1738000.004	1738000.000	**Magnesium**	0.00000
2700000.003	2700000.00	**Aluminum**	0.00000
2329999.999	2330000.000	**Silicon**	0.00000
1823000.007	1823000.0000	**Phosphorus**	0.00000
1960000.007	1960000.000	**Sulfur**	0.00000

Tablica 2.2.4. Comparison of empirical and calculated values from pattern no 4 - Period IV

Calculation result	Experimental density	The name of the chemical element	Error [%]
857191.5786	856000.0000	**Potassium**	0.13901
1543470.141	1550000.00	**Calcium**	0.42128
2587461.756	2985000.00	**Scand**	13.31786
4545297.355	4507000.000	**Titanium**	0.84257
6092222.783	6110000.000	**Vanadium**	0.29095
6287251.578	7140000.000	**Chrome**	11.94326
7350083.178	7470000.000	**Manganese**	1.60531
7989039.467	7874000.000	**Iron**	1.43997
9570005.903	8900000.000	**Cobalt**	7.00110
9083920.833	8908000.000	**Nickel**	1.93662
8631707.491	8920000.0000	**Copper**	3.23198
7087377.675	7140000.000	**Zinc**	0.73701
6179405.842	5904000.000	**Gal**	4.45683
5153063.273	5323000.000	**Germanium**	3.19250
5768137.989	5727000.000	**Arsenic**	0.71319

Tablica 2.2.5. Comparison of empirical and calculated values from pattern no 4 - Period V

Calculation result	Experimental density	The name of the chemical element	Error [%]
1534995.969	1532000.000	**Rubidium**	0.19518
2613439.357	2630000.000	**Strontium**	0.62968
3897872.278	4472000.000	**Yttrium**	12.83828
6616336.088	6511000.000	**Zirconium**	1.59206
8472717.312	8570000.000	**Niobium**	1.13515
8874037.271	10280000.000	**Molybdenum**	13.67668

11398704.51	11500000.0	**Technetium**	0.88083
13496857.9	12370000.0	**Ruthenium**	8.34904
12663674.22	12450000.00	**Rhodium**	1.68730
11994280.32	12023000.00	**Palladium**	0.23887
8024626.75	10490000.00	**Silver**	23.50213
8500796.681	8650000.000	**Cadmium**	1.72489
7382922.377	7310000.000	**Indium**	0.98772
7358744.698	7310000.000	**Tin**	0.66241
6659511.391	6697000.000	**Antimony**	0.55978
6244265.339	6240000.000	**Tellurium**	0.06831

Tablica 2.2.6. Comparison of empirical and calculated values from pattern no 4 - Period VI

Calculation result	Experimental density	The name of the chemical element	Error [%]
1809976.662	1879000.000	**Cez**	3.67341
3860077.636	3510000.000	**Barium**	9.06919
5647609.827	6146000.000	**Lanthanum**	8.10918
6868088.942	6689000.0000	**Cerium**	2.60755
6921392.8	7010000.0000	**Praseodymium**	1.26401
7005037.943	7010000.000	**Neodymium**	0.07079
7078619.281	7353000.000	**Samarium**	3.73155
7071188.447	5244000.000	**Europium**	25.83991
7885991.371	7901000.000	**Gadolinium**	0.18996
8641167.365	8219000.000	**Terbium**	4.88554
8822579.456	8551000.00	**Dysprosium**	3.07823
8946321.747	8795000.00	**Holm**	1.69144
9054241.792	9066000.000	**Erbium**	0.12970
9104331.983	9321000.000	**Thulium**	2.32451
9257061.194	6570000.000	**Ytterbium**	29.02715
9262540	9841000.000	**Lutetium**	5.87806

13428499.85	13310000.00	**Hafnium**	0.88245
16410791.17	16650000.00	**Tantalum**	1.43669
20419959.75	19250000.0	**Tungsten**	5.72949
20527305.74	21020000.00	**Rhenium**	2.34393
23462445.65	22610000.00	**Osmium**	3.63323
21335825.38	22650000.00	**Iridium**	5.80210
22038465.3	21090000.00	**Platinum**	4.30368
22859539.97	19300000.00	**Gold**	15.57135
9105950.517	11850000.00	**Thallium**	23.15654
11146000.37	11340000.00	**Lead**	1.71076
16080904.41	9780000.00	**Bismuth**	39.18253
9261126.119	9196000.000	**Polonium**	0.70322

Tablica 2.2.7. Comparison of empirical and calculated values from pattern no 4 - Period VII

Calculation result	Experimental density	The name of the chemical element	Error [%]
5000002.293	5000000	**Rad**	0.0000
11724003.95	11724000	**Thorium**	0.0000
15370004.16	15370000	**Proactin**	0.0000
19050004.62	19050000	**Uranium**	0.0000
20450004.1	20450000	**Neptunium**	0.0000
19816003.21	19816000	**Plutonium**	0.0000

Based on the conducted research, it can be concluded that there is a large correlation between the atomic structure of the elements and their physicochemical properties, in this case density. Thanks to the proposed formula, it was possible to determine their density with high accuracy. The analysis carried out by the author show that the presented theoretical model allows to determine the density of materials for a large group of pure elements with high accuracy. Comparing it with many other models, especially for assessing other physical properties, e.g. viscosities, which are often semi-empirical models, achieve quite satisfactory results. Many other models target only a specific group of materials, with significant deviations

from the actual values [34, 35, 36]. The presented model is also aimed at a relatively narrow group of materials, as it concerns metal elements, semi-metals or non-metals in the solid state, in pure form. It should be noted, however, that this model only uses information about the atomic structure of elements, such as atomic number, number of atomic shells, atomic radius, and absolute atomic mass.

Summing up the considerations related to the above model, it is worth looking at the group of elements to which the lanthanides will belong. These elements are largely similar to each other (in terms of the parameters contained in the model). Two elements from this group, however, show significant calculation errors of 20-30%. These include Yterb and Europ. Analysing the structure of these elements further, it can be seen that the density of matter can also be influenced by electron orbitals, each of which has its own energy level and its own properties. Electron orbitals are described e.g. the orbital moment quantum number (e), the magnetic quantum number (m) and the principal quantum number (n). It turns out that these two elements have the same properties, i.e. e = 3, m = 3 and n = 4, which may indicate the influence of the true density of matter.

The presented theoretical model can be improved by adapting it to determine the density at a given temperature according to the relationship:

$$\rho(T) = \frac{\rho_{STP}}{\Delta T \cdot \beta + 1} \left[\frac{\frac{kg}{m^3}}{K \cdot \frac{1}{K}} = \frac{kg}{m^3} \right] \quad (5)$$

where:
$\rho(T)$ – density at a given temperature
ρ_{STP} – density under normal conditions
ΔT – the difference between the test temperature and the temperature of 273.15 K (0 °C)
β – coefficient of thermal expansion of the volume

It should be noted, however, that the values of the thermal expansion coefficient are values determined experimentally, not theoretically, therefore this dependence is a semi-empirical model [6].

An attempt to refer the presented model to the determination of the density of complex systems present in slag mixtures (e.g. from oxides) does not give such good results. Regardless of the approach to this issue, the results show large discrepancies. An example is silicon oxide SiO2. The simplest approach to determining its density would be to determine the

absolute molecular weight of the compound and determine the amount of occurrence of this type of molecules in a given volume. Determining the absolute molecular weight is quite simple (28.085 u + 2 · 15.999 u) · 1.66054 · 10^{-24} = 9.97702 · 10^{-23} grams. However, the volume occupied by a silicon oxide particle is not so easy to determine. The more so that this compound can crystallize in various crystal lattices and occur in the form of α quartz, β quartz, tridymite, cristobalite, or finally in the amorphous form. The crystal lattices it creates give regular structures, through rhombic, monoclinic, tetragonal, trigonal, ending with hexagonal. However, an attempt to relate the crystal lattice of the oxides with their density by means of proportionality coefficients also does not give the expected results. As we know, oxides can be of a different nature, form chemical compounds in different configurations with oxygen, and finally they can come from elements with very complex properties, which can lead to problems with presenting a simple mathematical model.

2.3 Viscosity of slags and alloys

The viscosity of the extraction coatings during the refining operation is one of the most important properties. The diffusion of impurities from the metal bath into the slag will be easier at low slag viscosity. It was described, among others Stockes formula (Einstein-Smoluchowski), indicating the relationship between the diffusion coefficient of impurities and the viscosity of the slag [37-42]:

$$D = \frac{R_g \cdot T}{6 \cdot \pi \cdot r_D \cdot N_a} \cdot \frac{1}{\eta} \quad (6)$$

where:
D – diffusion coefficient
R_g – gas constant (8,31 J/(mol*K))
T – temperature
r_D – the radius of the moving particle
N_a – Avogadro's number (6.022*10^{23} mol^{-1})
η-slag viscosity

As can be seen from the formula and other studies [7, 43, 41, 44-48], the viscosity of the slag will depend on the temperature of the system, but the interaction with the refined alloy and gases in the external atmosphere is also important, which especially contributes to the magnitude of the resulting slag. The low viscosity also has its drawbacks as it will be

corrosive to the kiln lining as well as making it difficult to remove the coating when poured into the ladle.

Due to the high-temperature nature of the process and the influence of external factors, the measurement of slag viscosity is a difficult task. One of the interesting methods proposed and patented by the AGH University of Science and Technology in Krakow is a method using concentric cylinders rotating after immersion in liquid slag placed in a heated chamber [49].

Over the years, many different methods have been developed to determine the viscosity of metallurgical slags. Particularly interesting are mathematical and semi-empirical methods that allow modelling of the described property. In an earlier work [6], the author presented 29 different models known from the literature, which allow to determine the viscosity of liquid slags, metals and multi-component solutions. In the case of modelling the properties of metallurgical slags, it is worth recalling the most important of them.

2.3.1 Moelwyn-Hughes model

In 1961, the Welsh chemist Emyr Alun Moelwyn-Hughes proposed one of the first models for determining the viscosity of alloys and metals described by the formula [150]:

$$\eta = (\eta_1 X_1 + \eta_2 X_2)\left(1 - 2\frac{H_m}{RT}\right) \qquad (7)$$

where:
η, η_1, η_2 – viscosity of alloys or metals
X_1, X_2 – mole fractions of metals
H_m – molar enthalpy of mixing of liquid alloys
R – gas constant
T – temperature

In the above case, we are dealing with a semi-empirical model, because the viscosity of the system is determined on the basis of the partial viscosity of the metals or alloys contained in it. In addition, the formula has been modified by the value of Hm, which refers to the molar enthalpy of mixing of liquid alloys. According to the definition [151], the enthalpy of mixtures characterizes them in terms of energy, but in non-electrolyte solutions where strong intermolecular interactions occur. The enthalpy of mixtures can be

taken to be the difference between the moles of components "i" before and after mixing:

$$\Delta H_{miesz} = H - \sum_{i=1}^{k} X_i H_i^0 = \sum X_i (H_i - H_i^0) \quad (8)$$

where:
H – the enthalpy of mixing of the resulting solution
H_i^0 – the molar enthalpy of component "i" before mixing
H_i – molar enthalpy of component "i" after mixing
X_i – mole fraction of component "i"

It is worth noting that the enthalpy of ideal solutions is zero. By ideal solutions we mean mixtures in which neither the volume nor the internal energy changes. Therefore, such solutions satisfy Raoult's law [152]. In addition, the relationship between the vapour pressure and the composition of the liquid is shown in the graph (Fig. 2.3.1.1) below:

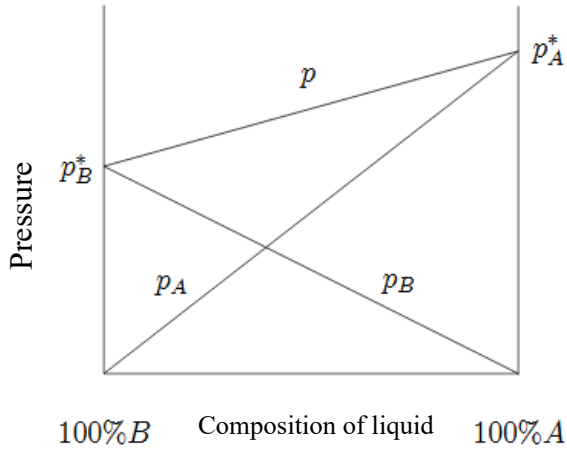

Fig 2.3.1.1. The total vapour pressure "p" above the solution and the partial pressures "pa" and "pb" as a function of liquid composition for solutions satisfying Raoult's law.

Summarizing the formula proposed by Moelwyn-Hughes, it can be concluded that there is a linear relationship between composition and viscosity in a given system. However, the condition must be fulfilled for which there are no strong intermolecular interactions in the solution and the enthalpy of mixing tends to zero. However, it is worth noting that, based on

the relevant data, the enthalpy of dissolution of a component in a solution can be calculated, as well as the decrease in thermodynamic potential as a function of temperature.

A good example is the introduction of chromium into liquid iron, where the decrease in thermodynamic potential will be determined as a function of temperature. The chromium that will be introduced into the system is solid. To determine the potential of a thermodynamic reaction, the melting and dissolving potential of a component in a solution must be determined. The following relationship can be used to determine the melting enthalpy:

$$\Delta G_{Top} = \Delta H_{Top} - \left(\frac{\Delta H_{Top}}{T_{Top}}\right) \cdot T$$

where for most metals: $\frac{\Delta H_{Top}}{T_{Top}} \approx 8{,}8$ (J/mol·K)

Since the value we are looking for is ΔHTop, while ΔGTop is normally equal to 0, we can write:

$$0 = \Delta H_{Top} - 8{,}8 \cdot T$$

$$\Delta H_{Top} = 8{,}8 \cdot 2130{,}15$$

$$\Delta H_{Top} = 18745.32 \text{ (J/gatom)}$$

Where the value 2130.15 refers to the melting point of chromium. Relating the obtained value to the above formula, the dependence of the melting potential as a function of temperature can be presented as:

$$\Delta G_{Top} = \Delta H_{Top} - \left(\frac{\Delta H_{Top}}{T_{Top}}\right) \cdot T$$

$$\Delta G_{Top} = 18745.32 - \left(\frac{18745.32}{2130.15}\right) \cdot T$$

$$\mathbf{\Delta G_{Top} = 18745.32 - 8.8 \cdot T \text{ (J/gatom)}}$$

The dissolution potential can be calculated using the relationship:

$$\Delta G_x = 19.147T \cdot \lg\frac{m_M \cdot f_x}{m_x \cdot 100}$$

If we assume that we are dealing with an ideal solution, then the activity coefficients f_x will be equal to 1, so we can write:

$$\Delta G_{Cr} = 19.47T \cdot \lg\frac{55,85}{52,01 \cdot 100} = \mathbf{-37.70 \cdot T\ (J/gatom)}$$

After adding the values of the above potentials together, we get the value:

$$\mathbf{\Delta G_{Cr} = 18745.32 - 46.5 \cdot T\ (J/gatom)}$$

Analysing the literature data, it can be seen that the chromium activity coefficient at a temperature above 1800 K is at the level of $f_{Cr} = 1.14$. Therefore, given this value in the example above, we can get:

$$\Delta G_{Cr} = 19300 - 46.8 \cdot T\ (J/gatom)$$

Further analysis of the example presented above shows that obtaining ideal solutions even in simple cases is very difficult and the activity coefficients are of key importance here. As a result, obtaining a fully linear characteristic of the system in the entire range of the percentage composition is basically impossible. However, it is possible to distinguish areas where the dependencies will be linear. An example is the dependence of the viscosity of the Ag-Sn alloy for different temperatures, which will change depending on the mass percentage of the components of the system. The figure (Fig. 2.3.1.2) below shows as many as 7 characteristic sections that make up the entire system [153]:

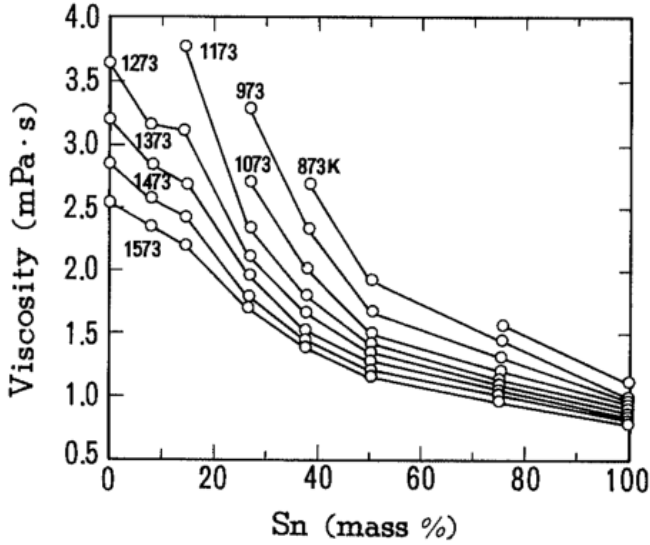

Fig. 2.3.1.2. Dependence of Ag – Sn alloy viscosity on its composition at different temperatures

2.3.2 Model of Iide, Ueda, Morita

In 1977, a team of scientists - Takamichi Iida, Mitsuru Ueda and Zenichiro Morita proposed a new formula for determining the viscosity of liquid metals and alloys. Despite the fact that it was a modification of the formula from 1961, it introduced a relationship between the physical properties (here viscosity) and the atomic structure of metals [154]. This has been described by the formula:

$$\Delta\eta = (X_1\eta_1 + X_2\eta_2)\left[-\frac{5X_1X_2(\sigma_1-\sigma_2)^2}{x_1\sigma_1^2 + x_2\sigma_2^2} + 2\left\{\sqrt{1+\frac{(X_1X_2\sqrt{m_1}-\sqrt{m_2})^2}{(X_1\sqrt{m_1}+X_2\sqrt{m_2})^2}}-1\right\} - \frac{0{,}12X_1X_2\Delta u}{kT}\right] \quad (9)$$