RESEARCH OVER SOME PHYSICAL-CHEMICAL PROCESSES TAKING PLACE IN THE SULPHOUROUS MINERAL WATERS FOR THE KNOWLEDGE OF THEIR QUALITIES ALTERATIONS OCCURRED IN TIME

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abstract: The present work is treating the physical-chemical alterations registered by the sulphurous waters. They register the redox phenomenon where participate the sulphur compounds in different states of oxidations, especially H_2S and HS^- ions in correlation with the pH, the temperature and the water composition.

Introduction

The sulphurous mineral waters represent complex solutions of electrolytes in which exists sulphur compounds in state of oxidation 2, i.e. H_2S, HS^-, and more rarely S^{2-}, which gives them specific characters reflected in the therapeutic effect.

The large possibilities of valorisation from the medical field have necessitated in the past and also request nowadays the attention over the physical-chemical composition and processes of this kind, with their direct reflection in the capacity of keeping the therapeutic characters.

The analytical data regarding the sulphurous waters accumulated over the years have put in emphasized o great variety of physical-chemical compounds both as regards quality and quantity. They have also emphasized and variations of the redox potential in time on some types of sulphurous waters as indicators of some characteristic processes of these solutions.

The present work is proposing itself the notification of the physical-chemical balances mobility in time of the sulphurous mineral waters, of the generating causes, as well for the determination of some correspondences between the physical-chemical indicators alteration and the therapeutical effects. The premise from where they start in the interpretation of these physical-chemical from these mineral waters is that they represent electrolytes solutions of a determined ionic strength, which have an evolution in time, strongly influenced by the interactions between the solution ions. The size of the ionic strength

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influences the activity coefficients of the existing ions and by these, the processes at which participate the ions in solution.

The *p*H is a value both dependant of the solution ionic strength and the temperature as well, fact to be considered in the values estimation. Its mobility in time in the sulphurous mineral waters is an indicator on the processes taking place in them and of which they mention:

– ionization phenomena as that where participate the H_2S

– salts hydrolyze phenomenon

– precipitation phenomenon (ex. the insolvable sulphurs formation)

– oxidation-reduction phenomenon of which they can mention the one with the participation of the sulphur compounds in different states of oxidation

Experiments

The water ionization process being an endothermic process, the dissociation degree is growing (in a sensible way), with the temperature rising. For a given temperature the water ionization is growing together the solution ionic strength.

The sulphurate hydrogen (H_2S) is soluble in water (the saturated solution contains at 20°C – 3.85g/l). In the watery solution this one is ionizing forming ions of hydrosulphur:

$$H_2S + H_2O \rightleftarrows H_3O + HS^-$$
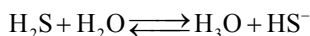
and a in reduced measure ions of sulphur S^{2-}

$$HS^- + H_2O \rightleftarrows H_3O + S^{2-}$$
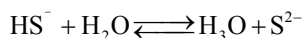
The above ionization balances are characterized by the quantities of acidity K_1 and K_2

$$K_1 = \frac{\left[HS^- \right]\left[H_3O^+ \right]}{\left[H_2S \right]} = 6.3 \times 10^{-8}$$

$$K_2 = \frac{\left[S^{2-} \right]\left[H_3O \right]}{\left[HS^- \right]} = 1.3 \times 10^{-12}$$

which demonstrates the weak acid character of the sulphurate hydrogen, weaker even in respect the carbonic acid.

The temperature manifests in this case too its influence over the ionization characters.

Egorov and Odinels indicate a calculation formula for the determination of the ionization constants related to the temperature.

$$-\log k = \frac{A}{T} + B$$

Where for the first ionization constant K_1, *A*=1132 and *B*=3,191.

The calculations have emphasized an increase of the K_1 values related to the temperature, which means an increase of the ionization phenomena as the temperature rises.

As regards the alkaline sulphurs and hydrosulphurs, the latter which exists in the sulphurous waters are partially hydrolyzed salts, as can be noticed in the equations below:

$$Na_2S + H_2O \rightleftharpoons NaSH + NaOH$$

respectively

$$NaSH + H_2O \rightleftharpoons H_2S + NaOH$$
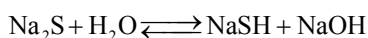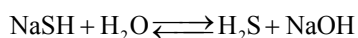
For this reason the watery solutions where are present sulphurs or hydrosulphurs have an alkaline character.

The presence in a solution of water and alkaline hydrosulphurs of the sulphurate hydrogen has an action of dabbering by the decrease of its pH. In this way the pH is determined by the coexistence of the two balances of hydrolysis of the hydrosulphurs and ionization of the weak H_2S acid, and thus influenced by the ration of the two compounds concentrations.

In a first approximation this dependence can be expressed by the formula:

$$\left[H^+ \right] = k\frac{a}{c}$$

where: k = the acid constant of dissociation; a = the acid concentration; c = the salt concentration

To the above mentioned phenomena they can add the possibility of some precipitation reactions which in the sulphurous waters have as result the formation of some insolvable salts, such as FeS, CuS, CoS, ZnS, NiS, etc. or of some hydroxides, such as Al (OH)$_3$, Cr (OH)$_3$ and under special situations Fe (OH)$_3$.

The precipitation of the above mentioned sulphurs is both determined by their products of solubility (ex. : P_{FeS} = 3.7×10^{-19}, P_{CoS} = 3.0×10^{-26}, P_{NiS} = 3.0×10^{-21},etc. as wells as by the solution pH.

It is worth to mention the fact that at pH-s close to 8 as those existent in the studied sulphurous waters, the concentration of the S^{2-} of the solution, calculated by the relation:

$$\left[S^{2-} \right] = \frac{k}{\left[H^+ \right]^2} = \frac{10^{-23}}{\left[H^+ \right]^2}$$

can determine the respective ions precipitation at their lowest concentrations. This is the explanation of the appearance of some deposits of black colour within the solutions of the sulphurous mineral waters, mainly on the basis of FeS.

As regards the redox processes within these mineral waters, they include the chemical alterations of the sulphur compounds in different states of oxidations.

The specialty literature emphasizes that the sulphurate hydrogen (H_2S) oxidation, and of its salts takes place gradually, the stability of the sulphur compounds being determined by the solution pH, the partial pressure of the oxygen and the temperature.

The presence of the SO_4^{2-} has a catalytic effect on the sulphurs oxidation.

The [H] research as regards the oxidation speed and mechanism by the atmospheric oxygen of H_2S, M_eSH and of their salts in a watery solution have emphasized that they are talking of a complex heterogeneous process determined by the diffusion coefficients of the compounds and the speed constants of the chemical reactions.

The oxidation speed is influenced by the temperature and the ionic compounds of the water, that is of the ionic strength of the solution; the reaction speed is growing generally together with the ionic strength.

At pH-s between 7 – 13.74 the main oxidation product is $S_2O_3^{2-}$ with the increase of pH, the formation of SO_4^{2-} being accentuated.

There are also to mention the studies regarding the formation of the polisulphurs in watery solutions. When the water containing sulphurs is exposed to air, the reaction between the suplhurs and the oxygen takes place slowly, the polisulphurs being a reaction intermediary.

The reaction speed is dependent on pH; generally the maximal concentration of polisulphur corresponding to the pH field 7.0 ±0.4 range, the reaction speed decreasing rapidly both in acid solution and in alkaline ones.

Under a pressure of 1 atm of the oxygen and a concentration in sulphurs of 10^{-3} – 10^{-2} H/l a conversion of 8 – 14% is attained.

They give below the reaction for the formation of the sodium disulphur:

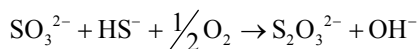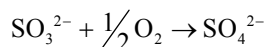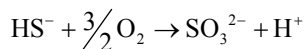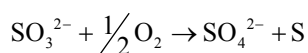$$2NaSH + \frac{1}{2}O_2 \rightleftharpoons NaS-SNa + H_2O$$
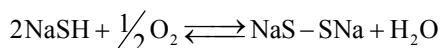
In watery solutions in the presence of oxygen the polisulphurs can oxide at the tiosulphate $S_2O_5^{2-}$ ions.

Regarding the significance of the redox potential of the natural waters they can appreciate that they are not balance potentials, the natural water not being a redox balance. The redox potential can be used only to foresee the direction of a reaction, but not its intensity.

In the context of the studies dedicated to the processes of oxidation of the sulphurate hydrogen and the hydrosulphurs of the watery solutions they mention too the ones of Avrahami and Golding for the situation of the small concentrations of these compounds.

The reactions indicated as taking place in solution are shown below:

$$HS^- + \frac{3}{2}O_2 \rightarrow SO_3^{2-} + H^+$$

$$SO_3^{2-} + \frac{1}{2}O_2 \rightarrow SO_4^{2-}$$

$$SO_3^{2-} + HS^- + \frac{1}{2}O_2 \rightarrow S_2O_3^{2-} + OH^-$$

$$SO_3^{2-} + \tfrac{1}{2}O_2 \rightarrow SO_4^{2-} + S$$

The oxidation speed has been increased by the *p*H and temperature increase. The first reaction is the determinant stage of speed, followed by the rapid transformations of the SO_3^{2-} ions and finally by the slow oxidation of the $S_2O_3^{2-}$ in SO_4^{2-} and S ions.

The self-oxidation of the sulphurs in watery solutions and the nature of the formed reaction products is dependant of the concentration:

[HS-] $< 2\times10^{-3}$ M, the self-oxidation is very slow and the reaction product is sulphur.

For concentrations of 2×10^{-3} M $<$ [HS$^-$] $< 3\times10^{-3}$ M, the main reaction products are represented by the polisulphurs, and at bigger concentrations of the HS$^-$, takes place a rapid oxidation of the sulphur at oxidated anions.

Even if there some valoric differences for the specification of the reaction products nature, remains as a conclusion the tendency of these compounds to oxide depending on the factors above mentioned at sulphur, polisulphurs and oxygenated anions, mainly $S_2O_3^{2-}$ and SO_4^{2-}.

The presentation I made has are a scope the creation of a guide with physical–chemical factors and processes which could possible take place in the sulphurous mineral waters, that could be useful in the interpretation of the phenomena experimental observed and the physical–chemical data obtained by experimental determinations.

Work Methodology

As regards the chemical analyze methodology, they use the volumetric methods of analyze, of H_2S, HS$^-$, $S_2O_3^-$, SO_3^{2-}, the gravimetric method for the determination of the SO_4^{2-} and the extraction of tricloretilene of the colloidal sulphur.

As regards the evaluation of the content in H_2S and HS$^-$, they can mention the use of the relation:

$$K_1 = \frac{\left[HS^-\right]\left[H_3O^+\right]}{\left[H_2S\right]} = 6.3\times10^{-8}$$

Taking into account the K values at different temperatures calculated with the relation:

$$-\log K = \tfrac{A}{T} + B$$

and the total concentration in mE/L of H_2S and HS$^-$ determined with the titrimetric method.

In case of the polisulphurs presence it is to be mentioned that the titrimetric method indicated the global concentration in H_2S, HS$^-$ and polisulphur anions, the reason for which it is recommended the presentation of the analytical data as mE/L of the sulphur compounds as anions in state of global oxidation "–2" and not as H_2S which do not correspond to the reality.

In order to emphasize the polisulphurs they have proceeded at the oxidation of the compounds with sulphur in the state of oxidation "−2" of the mineral water in sulphur and its extraction with tricloretilene.

Conclusions

The behaviour of the suplhurous waters in time is dependant of a series of physical–chemical factors, among which they can mention:

– the temperature at emergencies and its variation in time
– the chemical composition and respectively the ionic strength of the solution
– the concentrations of H_2S and HS^- and other sulphur compounds
– the partial pressure of oxygen
– the solution pH

The used methods of current analyze determine the total content in H_2S and HS^- and polisulphurs existing in mg H_2S/l.

Is more correct the expression of the results in mE/L anions of sulphur in state of global oxidation −2.

The waters with a high content in H_2S and a pH at the source between 7.4–7.6 have a bigger percentage of extractable colloidal sulphur, than the one corresponding to H_2S and HS^- and even $S_2O_3^{2-}$ indicating the presence of some anions richer in sulphur, such as polisulphurs.

In case of the polisulphurs absence they can estimate by calculation, depending on the temperature and ph the ration between H_2S and HS^-.

The redox phenomena can be determined by the oscillations of the $S_2O_3^{2-}$ anions, the increase of concentration in SO_4^{2-} and the deposits of colloidal sulphur.

The tendency of the sulphur compounds oxidation from the state of oxidation −2 (H_2S, HS^-, polisulphur) is closely correlated with their concentration and partial pressure of the oxygen.

They can observe an intensification of the phenomena of oxidation, at more alkaline pHs.

The capsulated probes, without the presence of an air volume above the liquid, have a smaller tendency of oxidation and this is no more limited al colloidal sulphur, but also at superior products of oxidation (oxygenated anions of sulphur).

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