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THE INFLUENCE OF TEMPERATURE AND PRESSURE ON PRECIPITATION AND SUBSEQUENT SCALE FORMATION OF BARIUM AND STRONTIUM SULPHATES DURING ENHANCED OIL RECOVERY PROCESSES

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Abstract. *Keeping the oil reservoir at high pressure to maximize production output and to avoid scale formation is the challenge for oil industries today. Injected water insert in the reservoirs usually comes from seawater due to practicability, low investment and ease of operation in relation to other fluids. It usually has a high concentration of sulphate ions. Formation water is the one trapped in the interstices of sedimentary rock of reservoirs. It presents considerable concentrations of alkaline and alkaline earth metals, such as barium and strontium. When these two waters are mixed, formation and precipitation of inorganic compounds may occur due to its incompatibility. Temperature and pressure also strongly influence precipitation, especially when it leads to supersaturation. Therefore, it is essential to understand the process that takes the precipitated particles to an eventual adhesion to the pipeline walls, a process so-called scale formation. In addition to causing stoppages on the production line, scaling requires the use of specific equipment that can reach values in the order of millions of dollars. In the present work, a methodology that has already been used successfully to predict precipitation and calcium carbonate scale is applied to barium and strontium sulphates. For a given salt solubilization capacity, the proposed model predicts precipitation and subsequent formation of barium and strontium sulphates scaling using thermodynamic equations of pressure, temperature, and concentration. When compared to other models and software, the approach presented proves to be a good choice.*

Keywords: *Enhanced oil recovery, Inorganic scale, Thermodynamics, Sulphates*

1. INTRODUCTION

The amount of produced water changes accordingly to reservoir conditions, pointing that the volume increases depending on the stage of recovery. Water is an undesired subproduct which is always linked to oil extraction; it demands proper disposal and treatment due to the fact that it can causa environmental damage due to the presence of contaminants such as oil itself and dissolved or suspended salts as Rosa et al., (2006) explains. Composition and volume of the produced water may change according to the depth and characteristics of the producing field and the enhanced oil recovery methods used, according to Thomas (2004). Olajire (2015) says in his work that the formation water, or connate water, is defined as the water that occupies the interstices of a sedimentary rock and presents considerable concentrations of alkaline and alkaline earth metals, such as barium, Ba^{2+}, strontium, Sr^{2+}, and calcium, Ca^{2+}. On the other hand, injection water is that injected into the reservoir through an injection well, during the enhanced oil recovery process, with the objective of maintaining the reservoir pressure high enough to achieve a better efficiency in the recovery of hydrocarbons, leading to an extension on the life of the well. If the injected water is sea water, with a high concentration of sulphate ions, $SO4^{2-}$, the formation and precipitation of inorganic compounds may occur due to its incompatibility when mixed with the formation water. After precipitation, the particles of the solute are free to group together and / or settle on some surface serving as a basis for more particles to group there, and this is the scale principle. Mahan (1972) says that for most solutes there is a known limit to the amount that can be dissolved in a fixed volume of any solvent. Öncül et al., (2005) say that if the solubilization capacity of a solute by a solvent is crossed, there is supersaturation and this is the main factor for precipitation. Two common ways of generating supersaturation are through temperature and pressure variation. Moghadasi et al., (2003) concluded that for both barium sulphate and strontium sulphate, solubility is affected by an increase in temperature, with an increase in the brine's ionic strength and an increase in pressure; however, the precipitation of such salts is more affected by temperature. It should be noted that the pressure effect may be present in the solubility of the salt and also in the synthesis reaction; and that the drop in temperature will lead to a decrease in solute solubility in the solvent and a reduction in pressure will generate evaporation of the solvent. Thus, supersaturation is the parameter that is directly related to the precipitation of salts, since a supersaturated solution has a higher ion concentration than would normally be possible under suitable thermodynamic conditions. The supersaturation of a solution is calculated by the saturation ratio, which indicates the balance between the dissolved salt mass and the precipitated salt mass. This value can be obtained through the quotient of the reaction or by the product of ionic activity; however, it should be noted that both are related to the solubility product constant. After analysing the saturation ratio, the scale index is calculated. Not always precipitation will turn into scales, as the scale is the adhesion of the precipitate on a surface. Moghadasi et al., (2003) point out that scales can occur at any point where there is supersaturation, and that variations in pressure and temperature in pure water, or the mixture of two incompatible waters have a lot of influence on such phenomenon. As the conditions in the well tend to high pressures and low temperatures, the variable temperature ends up becoming more important to be analysed, and this is corroborated by Moghadasi et al., (2003) and Merdhah and Yassin (2007). In this work, it is studied what are the thermodynamic conditions that govern the precipitation of the studied inorganic compounds and it is calculated what are the possibilities of that precipitate's particles becoming scales.

2. DEVELOPMENT AND RESULTS

The equilibrium constant *Keq* of a chemical reaction is expressed by Equation 1. It is composed by the stoichiometric coefficients νi, by the molar concentration of the chemical compounds Ai, by the difference in Gibbs free energy between the reactants and the products in their standard state for the reaction, ΔGr^0, by the universal constant of gases *R* and by temperature, in Kelvin, T_k. According to Prausnitz et al., (1999), equilibrium is a condition in which there are no variations in the properties of a system, implying the equality of potential properties that can trigger thermodynamic processes.

$$K_{eq} = \frac{[A_3]^{v_3}[A_4]^{v_4}}{[A_1]^{v_1}[A_2]^{v_2}} = \Pi_i[A_i]^{v_i} = \exp\left(-\frac{\Delta G_r^0}{RT_k}\right) \quad (1)$$

For systems that are out of equilibrium, thermodynamic processes are spontaneously established in order to restore the state of equilibrium. In general, the factors that determine a state of equilibrium are:

• Concentration, whose increase in the quantity of a species favours the reaction that consumes that species;
• Temperature, whose increase shifts the equilibrium in order to favour endothermic reactions;
• Pressure, the increase of which implies a reduction in the specific volume, and, consequently, increases the concentration in the system.

It is observed that although similar to Eq. (1), the reaction quotient as shown in Eq. (2) can be calculated whether or not it is in the equilibrium state, as the instantaneous concentration of the species in the system is considered.

$$Q_c = \frac{[A_3]^{v_3}[A_4]^{v_4}}{[A_1]^{v_1}[A_2]^{v_2}} = \Pi_i[A_i]^{v_i} \quad (2)$$

Therefore, it is possible to perform the following analysis:

• Qc > Keq: suggests that the amount of product present is greater than in equilibrium;
• Qc < Keq: suggests that the concentration of reagents is greater than in equilibrium;
• Qc = Keq: suggests that the reaction is in equilibrium.

Rocha et al., (2001) show that when the systems are considerably saline, the effective concentration of the ion that can react is considered. For this, the property called species activity, *ai*, is used, which can be determined through Eq. (3) as a function of the concentration *Ai* and the activity coefficient of species γi, which is generally less than the unit.

$$a_i = \gamma_i[A_i] \quad (3)$$

Equation 4 relates the activity coefficient of the species γi to the equilibrium constant *Keq* and the solubility constant *Ksp*.

$$K_{sp} = \Pi_i K_{eq} {\gamma_i}^{v_i} \quad (4)$$

If the system is considered "ideal", as it is being considered in this study, the activity coefficient is unitary and, consequently, the activity will be equal to the concentration. For this type of situation, the equilibrium constant *Keq* is equal to the solubility constant *Ksp*.

Supersaturation is the property that is directly related to the precipitation of salts, being quantified by the saturation ratio *RS*, which indicates the equilibrium between the dissolved salt mass and the precipitated salt mass. Equation 5 defines *RS* through the quotient of the reaction *Qc*, by the solubility constant *Ksp*. It can be defined that:

• *RS*> 1: the solution is supersaturated and precipitation may occur
• *RS* = 1: the solution is saturated, that is, the maximum amount of salt is dissolved;
• *RS* <1: the solution is unsaturated, and dissolution may occur.

$$RS = \frac{Q_c}{K_{sp}} \quad (5)$$

The next step is to calculate the scale index. As explained before, not every precipitation becomes scales; in order to determine the possibility of scales formation, Eq. (6) is used. It defines *SI* through the logarithm of *RS* and can be defined as shown below:

• *SI* < 0 Potential for dissolution of pre-existing deposits
• *SI* = 0 No dissolution potential and no deposition potential
• *SI* > 0 Precipitation potential of solid deposits

$$SI = \log RS \quad (6)$$

The determination of the equilibrium constant of the reaction is essential for the subsequent evaluation of the supersaturation condition. The dependence of Keq on the thermodynamic conditions depends on the nature of each reaction. Changes in the temperature of a system contribute to the variation in the solubility of the salts and, therefore, reflect in the rate of supersaturation of the solution. Merdhah and Yassin (2007) show in their work that the increase and decrease in temperature can favour the solubility of salt, depending on the system. In this work, thermodynamic models are discussed to evaluate the effect of the temperature and pressure variation in *Keq*.

Langmuir (1997) starts from a system in equilibrium with a reference temperature Tk_{ref}, a reference pressure *Pref* and a reference equilibrium constant Keq_{ref} and considers two types of changes, one using constant temperature and one using constant pressure, reaching a final state with a pressure *P*, a temperature *Tk* and an equilibrium constant *Keq*. For each type of change an equation is established, these are known as Van't Hoff equations and are explained in Eq. (7) and Eq. (8).

$$\left(\frac{\partial lnK_{eq}}{\partial P}\right)_{T_K} = \frac{\Delta V_r^0}{RT_K} \Rightarrow ln\frac{K_{eq}}{K_{eq,ref}} = -\frac{\Delta V_r^0}{RT_K}\left[P - P_{ref}\right] \quad (7)$$

$$\frac{dlnK_{eq}}{dT_K} = \frac{\Delta H_r^0}{RT_k^2} \Rightarrow ln\frac{K_{eq}}{K_{eq,ref}} = -\frac{\Delta H_r^0}{R}\left[\frac{1}{T_K} - \frac{1}{T_{K,ref}}\right] \quad (8)$$

The influence of temperature on the formation of precipitate arises from the combination of the first and second laws of thermodynamics, through Gibbs free energy, through which it is possible to make a connection between the properties of individual substances and the extent to which the reactions take place. In the literature, there are a variety of thermodynamic models that propose expressions for such a combination, being presented in Table 1 with the due applicability for barium sulphate and/or strontium sulphate and discussed next.

Also, according to Langmuir (1997), endothermic reactions absorb heat in the direct reaction, thus favouring the reverse reaction with increasing temperature and causing the equilibrium constant to increase with increasing temperature. Thus, analysing the Van't Hoff equation, it is possible to observe that the change in the equilibrium constant *Keq* due to the temperature variation ΔTk is proportional to the magnitude of the reaction enthalpy ΔHr^o, generating a strong dependence on the equilibrium constant *Keq* with the temperature *Tk*.

For cases in which the reaction enthalpy ΔHr^o varies with temperature *Tk*, as a consequence of the dependence on specific heat *Cp* and pressure *P* with temperature *Tk*, the expanded Van't Hoff equation, presented in Eq. (9), must be used, with ΔCp_r^0 being the specific heat variation.

Among other models that can be used to calculate solubility constants, it is noteworthy the work of Haas and Fisher (1976) for strontium sulphate applied at temperatures between 10 °C and 90 °C, presented by Eq. (10), from the Table 1. In addition, Blount (1977) presents a correlation obtained experimentally for barium sulphate in a pure water solution as a function of temperature at the saturation pressure applicable at temperatures up to 300 °C, as shown by Eq. (11) on Table 1. Langmuir (1997) proposes an empirical equation for calculating the equilibrium constant, shown in Eq. (12) on Table 1, as a function of temperature Tk. The empirical constants A, B, C. D, E and G are listed in Table 2 for barium sulphate and strontium sulphate. Finally, Monnin (1999) presents an expression for strontium sulphate in Eq. (13).

Table 1. Thermodynamic models to evaluate the effect of temperature variation on the solubility constant *Ksp*.

Model	Salt	Equation	N
Van't Hoff	$BaSO_4$ $SrSO_4$	$\frac{dlnK_{eq}}{dT_K} = \frac{\Delta H_r^0}{RT_K^2}$	8
extended Van't Hoff	$BaSO_4$ $SrSO_4$	$logK_{sp}(T_K) = logK_{sp,ref}(T_{K,ref}) - \frac{\Delta H_r^0}{Rln10}\left(\frac{1}{T_K} - \frac{1}{T_{K,ref}}\right) + \frac{\Delta Cp_r^0}{R}\left[\frac{1}{ln10}\left(\frac{T_K}{T_{K,ref}} - 1\right) - log\frac{T_K}{T_{K,ref}}\right]$	9
Haas and Fischer (1976)	$SrSO_4$	$-logK_{sp} = 14805{,}9622 + 2{,}4660924T + \frac{40553604}{T^2} - 5436{,}3588logT - \frac{756968{,}533}{T}$	10
Blount (1977)	$BaSO_4$	$lnK_{sp}(T_K, P_{sat}) = 275{,}053 - 43{,}014lnT_K - \frac{15806{,}3}{T_K}$	11
Langmuir (1997)	$BaSO_4$ $SrSO_4$	$logK_{sp} = A + BT_K + \frac{C}{T_K} + DlogT_K + ET_k^2 + \frac{F}{T_k^2} + GT_k^{1/2}$	12
Monnin (1999)	$SrSO_4$	$lnK_{sp}(T_K, P_0) = 224{,}069 - 35{,}9422lnT_K - \frac{10302{,}32}{T_K}$	13

Source: Made by the author.

Table 2. Empirical constants of Equation 11.

Salt	A	B	C	D	E	F	G
$BaSO_4$	136,035	0	-7680,41	-48,595	0	0	0
$SrSO_4$	137,555	0	-6530,75	-6530,75	0	0	0

Source: Langmuir (1997).

To evaluate the effect of pressure variation in the calculation of the solubility constant, the thermodynamic models listed in Table 3 can be used. According to Langmuir (1997), the effect of the pressure change on the value of the equilibrium constant is proportional to the variation of the molar volume of the reaction, where all reagents and products are in the standard state, according to Eq. (7). However, this equation is applied when the difference between the molar volumes of the reagents and products in their standard states, ΔV_r^0, do not vary with the pressure in the range of interest. If ΔV_r^0 varies with the pressure difference, Eq. (14) should be used in which the difference between partial molar compressibility is considered, $\overline{\Delta K_r^0}$. Alternatively, Aggarwal et al., (1990) proposed Eq. (15) to estimate the effect of pressure on the solubility constant. In addition to these models, Blount (1977) carried out an experimental analysis in order to find data on solubility at high temperatures and pressures of pure barium sulphate, in aqueous solution and in sodium chloride, NaCl. At the end of his work, he presented Eq. (16), which presents the combined effect of both properties on the equilibrium constant of barium sulphate.

Table 3. Thermodynamic models for evaluating the effect of pressure variation on the solubility constant *Ksp*.

Model	Salt	Equation	N
Van´t Hoff	$BaSO_4$ $SrSO_4$	$\left(\frac{\partial lnK_{eq}}{\partial P}\right)_{T_K} = \frac{\Delta V_r^0}{RT_K}$	7
Van´t Hoff	$BaSO_4$ $SrSO_4$	$ln\frac{K_{sp,P}}{K_{sp,ref}} = -\frac{\Delta V_r^0 P}{RT_K} + \frac{\overline{\Delta K_r^0}P^2}{2RT_K}$	14
Aggarwal et al., (1990)	$BaSO_4$ $SrSO_4$	$ln\left(\frac{K_{sp,P}}{K_{sp,ref}}\right) = -\frac{\Delta V_r^0}{RT_{K,H_2O}^0} ln\left(\frac{\rho_{H_2O(P)}}{\rho_{H_2O,ref}^0}\right)$	15
Blount (1977)	$BaSO_4$	$log\,K_{eq} = (1{,}49325.10^{-2}.P - 48{,}61).log\,T_K + \frac{(2{,}3536.P - 7682{,}76)}{T_K} - 4{,}398.10^{-2}.P + 136{,}079$	16

Source: Made by the author.

For the barium sulphate, Moghadasi et al., (2003) concluded that solubility is affected by temperature increase, by the increase in the ionic strength of the brine and by the increase in pressure; however, the salt precipitation is more impacted by temperature. It is important to highlight that precipitation and solubility are different phenomenon and, therefore, they suffer different influences of thermodynamic parameters like temperature and pressure. For the strontium sulphate, Moghadasi et al., (2003) concluded that it normally, in addition to forming concomitantly with barium sulphate, is affected by the same variables; nonetheless it is more soluble.

Notably, in order to apply equations described in Table 1, it is necessary to have knowledge about the behaviour of the thermodynamic properties with temperature, such as Gibbs free energy, ΔG^o, specific heat under constant pressure ΔCp_r^0 and enthalpy ΔH_r^0. In literature, there are a lot of methodologies proposed to estimate these variables, such as using computational program SUPCRT92, as it is presented in the work of Johnson et al., (1992).

For this present work, Eq. (9) was applied to get the results shown in Table 1, it means that expanded Van't Hoff equation considers temperature variations. In a previous work, Cosmo (2013) used this same equation to predict the thermodynamic conditions that result in calcium carbonate scaled, obtaining good results. Another essential point for using this equation is to fill the constants related with specific heat, enthalpy variation and Gibbs free energy variation with reliable data. For this current work, for both compounds, were used data presented by Dean (1999) for a base temperature of 25°C as it is possible to verify in Table 4; then, the equation was feed with temperature variations from this.

Table 4. Thermodynamic properties for barium sulphate.

Salts and its reactions	$\Delta H_f^0 \left[\frac{KJ}{Mol}\right]$	$\Delta G_f^0 \left[\frac{KJ}{Mol}\right]$	$\Delta Cp_f^0 \left[\frac{KJ}{Mol.K}\right]$	$R \left[\frac{KJ}{Mol.K}\right]$
Ba^{2+}	-537,64	-560,74	0,0281	
SO_4^{2-}	-909,34	-744,5	-0,293	
$BaSO_4$	-1473,19	-1362,2	0,10175	
Reaction $Ba^{2+} + SO_4^{2-} \leftrightarrow BaSO_4$	26,21	56,96	-0,36665	0,008314462
Sr^{2+}	-545,8	-559,44	0,027	
$SrSO_4$	-1453,1	-1341	0,108	
Reaction $Sr^{2+} + SO_4^{2-} \leftrightarrow SrSO_4$	-1,97	36,93	-0,37399	

Source: Dean (1999).

Saturation curves were generated to barium sulphate relating temperature and equilibrium constant using methodologies presented in Eq. (9), Eq. (11) and Eq. (12) as well as the software SUPCRT92 and Geochemist's Workbench – GWB. In the GWB, barium sulphate and strontium sulphate were added as salts to be analysed and a saturation curve was generated considering a temperature range from 0°C to 100°C; it is important to highlight that the software was set in a way where activity constant was considered unitary. In the software SUPCRT92, it was necessary to enter with reactions $Ba^{2+} + SO_4^{2-} \leftrightarrow BaSO_4$ and $Sr^{2+} + SO_4^{2-} \leftrightarrow SrSO_4$ and a temperature interval from 25°C to 0°C and from 25°C to 100°C, the pressure variation used was from 1 Bar to 100 Bar; the result was a saturation curve relating salt solubility for each temperature and pressure. The activity coefficient used was also unitary. Results for barium sulphate are presented in Figure 1, being notable that the saturation curve obtained by Equation 9 converges for specific models, Eq. (11) and Eq. (12), as well as results obtained by software.

After using proposed values by different author to feed specific heat constant, enthalpy variation and Gibbs free energy variation in Equation 8, it was possible to discover that values suggested by Dean (1999) result in a curve with low percentage values, which varies from 0.01% to 0.1%; it means that these values are more suitable to be applied as their deviation are very small. For both barium sulphate and strontium sulphate, calculations using Equation 9 were done considering temperature variation from 0°C to 100°C and pressure as 1 Atm; as mentioned previously, a temperature of 25°C was used as base value and result was extrapolated to smaller and greater temperature values.

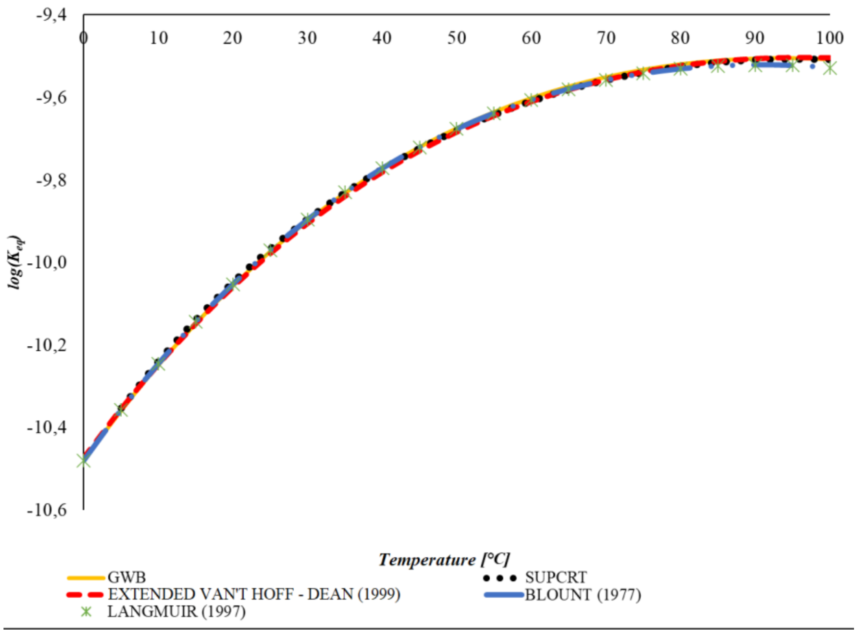

Figure 1. Saturation curve between the K_{eq} equilibrium constant and the temperature [°C] for barium sulphate.

To the strontium sulphate, also using values presented by Dean (1999) for specific heat, enthalpy variation and Gibbs free energy variation, and then applying them in Eq. (8), it is noteworthy that results vary from 0.13% to 0.62% when compared with results obtained by GWB software; which means that errors are really small. When these results are compared with other generated by specific models proposed by Eq. (9) and Eq. (12), errors are above of 2%, showing a difference between these values. Software SUPCRT92 generated a saturation curve with a lot of discrepancy in values, so this was not considered. Saturation curves that relate equilibrium constant with temperature for strontium sulphate are presented in Figure 2. It is possible to see that saturation curves do not converge, being disparate between specific models and results generated by GWB software.

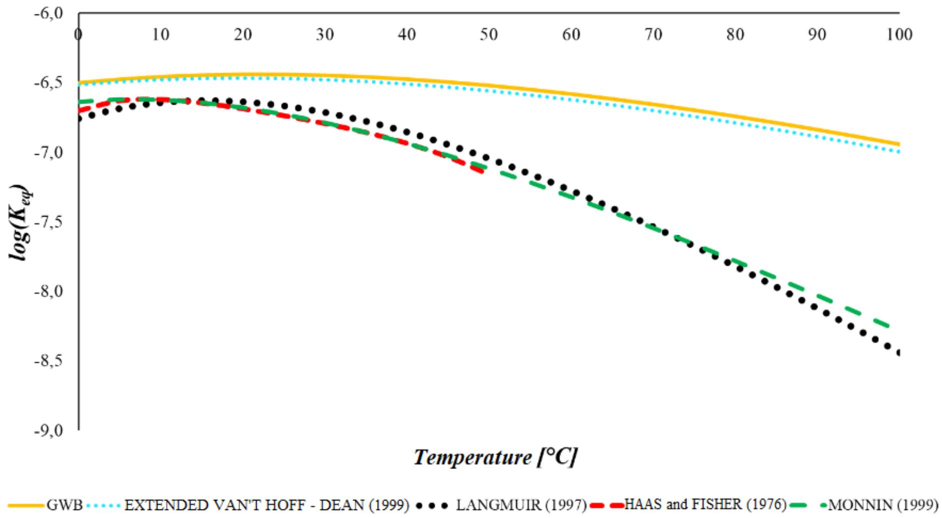

Figure 2. Saturation curve between the equilibrium constant K_{eq} and the temperature [°C] for strontium sulphate.

Results for both compounds are under comparison with results generated by the software Multiscale, which is a reference software for saline scales studies. The pressure effect in the equilibrium constant was verified for barium and strontium sulphates using Aggarwal et al (1990) equation, presented in Eq. (15). The molar volume of reaction was calculated by Eq. (17), obtained in work of Blount (1977). Other fundamental variables for the application of the equation of Aggarwal et al., (1990) were obtained from the work of Chen et al., (1977), as shown in Table 5.

$$\Delta V^0_{r,ref} = \frac{-1{,}377.10^5}{T_K} - 1{,}20391.T_K + 767{,}58 \quad (17)$$

Table 5. Parameters involved in the effect of pressure on the equilibrium constant, applied to Equation 15.

Parameter Equation	N
$\kappa^{T}_{H_2O}(P_{atm}, T_{ºC}) = \frac{k\prime_w - 1{,}01325^2.B\prime.(P_{atm}-1)^2}{k_w[k_w - 1{,}01325.(P_{atm}-1)]}$	15.1
$\rho_{H_2O}(T_C) = 0{,}99983952 + 6{,}78826.10^{-5}.T_C - 9{,}08659.10^{-6}.{T_C}^2 + 1{,}02213.10^{-7}.{T_C}^3 - 1{,}35439.10^{-9}.{T_C}^4 + 1{,}47115.10^{-11}.{T_C}^5 - 1{,}1166310^{-13}.{T_C}^6 + 5{,}04407.10^{-16}.{T_C}^7 - 1{,}00659.10^{-18}.{T_C}^8$	15.2
$\rho_{H_2O}(T_C.P_{atm}) = \frac{\rho_{H_2O}(T_C)}{\left(1 - \frac{1{,}01325(P_{atm}-1)}{k_w}\right)}$	15.3
$k_w = k'_w + 1{,}01325.A'(P_{atm} - 1) + 1{,}01325^2.B'(P_{atm} - 1)^2$	15.4
${k_w}' = 19652{,}17 + 148{,}183.T_C - 2{,}29995.{T_C}^2 + 0{,}01281.{T_C}^3 - 4{,}91564.10^{-5}.{T_C}^4 + 1{,}035531.10^{-7}.{T_C}^4$	15.5
$A' = 3{,}26138 + 5{,}223.10^{-4}.T_C + 1{,}324.10^{-4}.{T_C}^2 - 7{,}665.10^{-7}.{T_C}^3 + 8{,}584.10^{-10}.{T_C}^4$	15.6
$B' = 7{,}2061.10^{-5} - 5{,}8948.10^{-6}.T_C + 8{,}699.10^{-8}.{T_C}^2 - -1{,}01.10^{-9}.{T_C}^3 + 4{,}322.10^{-12}.{T_C}^4$	15.7

Source: Chen et al., (1977).

In order to better understand the influence of pressure on the Equilibrium Constant *Keq* for both barium and strontium sulphates, a comparison of values was made varying pressure from 1 bar to 100 bar for three different temperatures, 10°C, 50°C and 100°C. These values are presented on Table 6; it is clear that pressure has a prominent influence for strontium sulphate than for barium sulphate.

Table 6. Influence of pressure for barium and strontium sulphates.

Temperature [°C]	Barium Sulphate		Strontium Sulphate	
	Pressure [Bar]	Methodology	Pressure [Bar]	Methodology
10	1	-10,248	1	-6,48
	10	-10,238	10	-6,41
	10x	-0,10%	10x	-1,1%
	20	-10,228	20	-6,33
	20x	-0,20%	20x	-2,3%
	50	-10,195	50	-6,09
	50x	-0,52%	50x	-6,0%
	100	-10,140	100	-5,68
	100x	-1,07%	100x	-12,3%
50	1	-9,684	1	-6,56
	10	-9,677	10	-6,50
	10x	-0,07%	10x	-0,8%
	20	-9,670	20	-6,44
	20x	-0,15%	20x	-1,8%
	50	-9,647	50	-6,26
	50x	-0,39%	50x	-4,5%
	100	-9,608	100	-5,95
	100x	-0,79%	100x	-9,2%
100	1	-9,504	1	-7,00
	10	-9,498	10	-6,95
	10x	-0,07%	10x	-0,7%
	20	-9,491	20	-6,89
	20x	-0,14%	20x	-1,5%
	50	-9,470	50	-6,72
	50x	-0,37%	50x	-4,0%
	100	-9,434	100	-6,42
	100x	-0,75%	100x	-8,2%

Source: Made by the author.

Figures 3a and 3b graphically show the relation between the logarithm of the equilibrium constant, log*Keq*, and pressure for barium sulphate and strontium sulphate, respectively, using various temperatures.

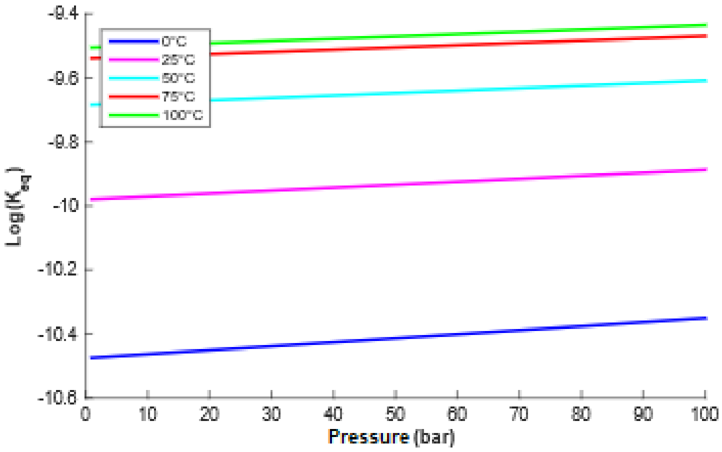

Figure 3a. Effect of pressure on the logarithm of the equilibrium constant for barium sulphate at various temperatures.

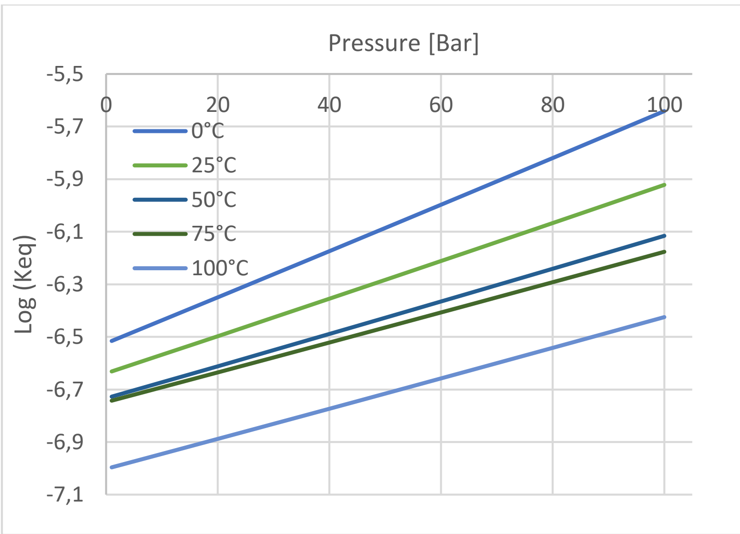

Figure 3b. Effect of pressure on the logarithm of the equilibrium constant for strontium sulphate at various temperatures.

Finally, solubility maps are made. It puts together the influence of temperature and pressure on the logarithm of the equilibrium constant for barium and strontium sulphate, respectively, resulting on figures 4a e 4b.

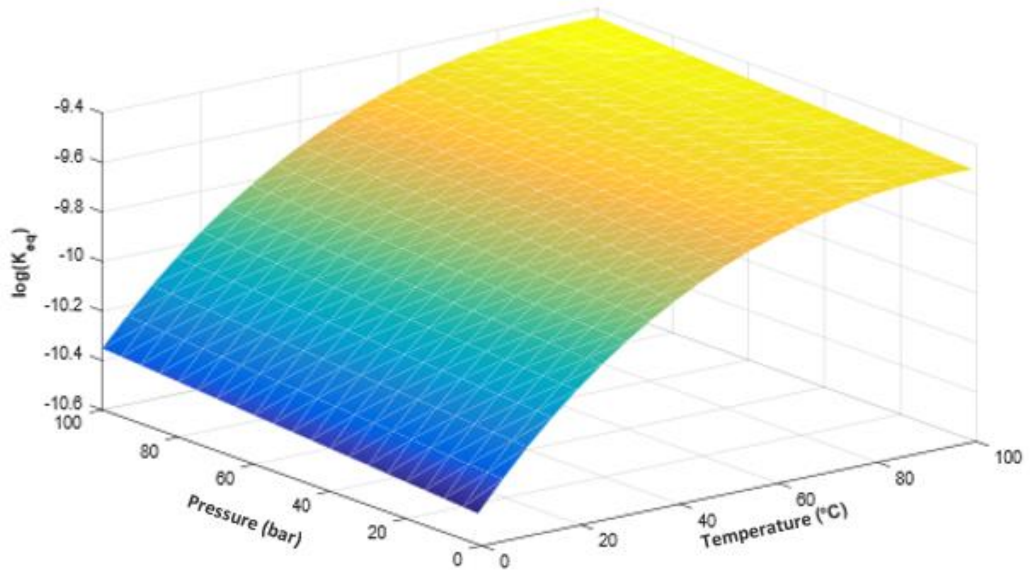

Figure 4a. Representation of the combined effect of temperature and pressure in the logarithm of the barium sulphate equilibrium constant.

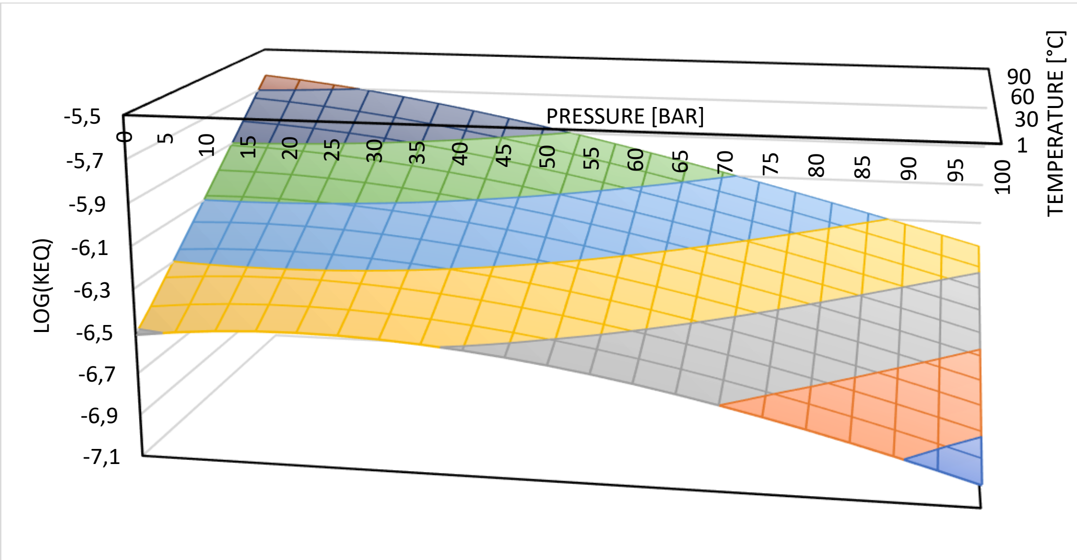

Figure 4b. Representation of the combined effect of temperature and pressure in the logarithm of the strontium sulphate equilibrium constant.

3. CONCLUSION

The extended equation of Van't Hoff has proved extremely useful to predict thermodynamic conditions related to the influence of temperature on the equilibrium constant for barium sulphate and for strontium sulphate, it generates reliable results when compared with specific models and software from the area. The equation proposed by Aggarwal et al (1990), which relates the influence of pressure on the equilibrium constant for barium sulphate and for strontium sulphate, results on data that must be better studied, comparing it with results generated by other models and software. Besides the fact that any newest data for the thermodynamics properties were not found, results relating the influence of temperature and pressure on the equilibrium constant for barium sulphate and for strontium sulphate points to be very promising. Currently, there are ongoing studies to determine the activity coefficient and also the quantity of precipitated mass of barium sulphate and strontium sulphate; this will allow the distinguishment of equilibrium constant and solubility constant, implying in closer results of reality and also the mass quantity that precipitates due to thermodynamic factors presented on this work. Another really important point is the results comparation between values gathered with the methodology presented on this work and the ones generated by the Multiscale software for barium sulphate and strontium sulphate; this software is considered really confident and the comparisons are already ongoing as well.

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