The Activity Coefficients and Equilibrium Constants of Commercial Potash at Temperature From 25 to 70°C

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Abstract: The activity coefficients and equilibrium constant of commercial potash produced by the APC in Jordan were estimated using the Pitzer's model. The equilibrium constant was found to correlate with saturation temperature using the equation ($K_{sp} = 0.3505\ T(°C)$). Good agreement was found between the estimated values of K_{sp} in this study and those estimated previously for the system $KCl.H_2O$ at temperatures below 40°C. More deviations were detected at higher temperatures.

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1. Introduction

Potassium chloride (Potash (KCl)) is an essential component of fertilizers that are used in the food production all over the world. The enhancement rate of food production is largely dependent upon fertilizers. In Jordan, the industry of KCl began in the early 1980s at the Arab Potash Company (APC), which utilizes highly concentrated natural brine obtained from the Dead Sea depending on solar energy for evaporation of water followed by a multi-stage crystallization process to produce the Potash. The composition of the commercial grade potash produced by APC is approximately as follows:96.75 wt % KCl, 2.82 wt % NaCl, 0.40 wt % $MgCl_2$, and 0.03 wt % $CaCl_2$.

It is clear that successful processing of the brine to produce potash is founded upon rigid knowledge of many thermodynamic properties of both brine and the potash itself. The equilibrium solubility constant and the activity coefficient are very essential to predict the solubility of minerals in the brine. The solubility of minerals in dilute aqueous solution has been extensively investigated previously both experimentally and theoretically by many researchers. The prediction of the thermodynamic properties of strong aqueous multicomponent electrolytes have received less attention despite of the great importance of such systems in many industries such as the production of potash. In this field, most of the work has been experimental. The studies consisted primarily of solubility measurement and different temperatures and concentrations Vant Hoff *et al. [1]*, and D'ans [2,3] studied the marine evaporites and they were able to measure the solubility at various temperatures and concentrations. Later, Hardie and Eugster [4] analyzed the solution mineral equilibria in terms of phase diagrams. After that, efforts were directed towards formulating a model based on both experimental and theoretical aspects capable of predicting the activity coefficient in multicomponent strong electrolyte mixtures. Moreover, some methods were proposed in this field that are based on the calculation of activity coefficients of single salt solutions accompanied by the application of certain mixing rules. Wood [5,6] developed a model for concentrated brines capable of predicting the solubilities of many of the common evaporite minerals in chloro-sulfate brines at 25°C and 1 atm. In this model an expression for calculating the activity coefficient of ore salt in water and another expression for calculating the water activity were formulated. Zemaitis *et al.*, [7] listed some other methods which belong to the last mentioned approach, namely:

1. Guggenheim: an equation using one parameter per ion pair.
2. Bromley: an equation using one parameter per ion pair.
3. Meissner: an Equation using one parameter per ion pair
4. Pitzer: an equation using three to four parameters per ion pair, one parameter for each like charged ion pair and one ternary interaction pair.

In general, the solubility of salts can be calculated once the activity coefficients and the equilibrium solubility constants are obtained.

Ferrando *et.al.,* [8] presented the mean activity coefficients of the NaCl and $CaCl_2$ salts obtained using the Pitzer [9-12] and Bromley [13] models by comparing the predicted data with the experimental data of Robinson and Stokesb[14]. Hence, Ferrando *et.al.* [8] has shown that the best predictions are obtained with Pitzer equations; this is due to the fact that the parameters of the modified Bromley model have been fitted by Jager [15] using mainly experimental water activity data rather than salt activity.

The objective of this study is to determine the solubility equilibrium constant of the commercial potash produced by APC in the temperature range (25 -70°C) using Pitzer's method [9,10]; which is used to calculate the mean ionic activity coefficient of KCl and of the trace salts associated with it.

2. Theory

In 1887, Arrhenius presented his theory of electrolytic dissociation of weak electrolytes in diluted solutions. This theory states that the dissociated ions of these electrolytes in the solution are in a state of chaotic motion similar to that of an ideal gas and that the interaction of ions in a solution does not affect their distribution and motion. The most significant advance in electrochemistry was made by Debye and Hückel [16]. Their treatment of ion-ion interaction led them to an exploration of the properties of relatively diluted solutions less than 0.01 M. The basic principle which they realized in their study was a consequence of the existence of an oppositely charged ionic atmosphere surrounding each ion, dilution of a solution involves work against the electrostatic attraction, in addition to the free energy of dilution for an ideal solution which is determined only by the decrease of ionic concentration. The difference between actual and ideal free energy changes is a measure of the activity coefficient of the particular ion in the given solution [17]. Due to their extensive work in this field they found it possible to calculate the activity coefficient, which is the ratio of the activity to the concentration of an ion, in dilute solution. Debye-Hückel [16] developed an equation to calculate the activity coefficient of an electrolyte, this equation was then known as Debye-Hückel limiting law:

$$\log(\gamma_{\mp}) = -A * |Z_+ * Z_-|\sqrt{I} \qquad (1)$$

where;

$\gamma_{\mp}$: is the mean molal activity coefficient of an electrolyte

A : is the Debye-Hückel constant which is temperature dependent

Z_+: is the number of charges on a cation

Z_-: is the number if charges on an anion

I: is the ionic strength in molality scale:

$$I = \frac{1}{2}\sum_i m_i * Z_i \qquad (2)$$

m_i is the ionic molality of anion *i*

$$A = \frac{1}{2.303} * \left(\frac{e}{\sqrt{D\,k\,T}}\right)^3 * \sqrt{\frac{2\,\pi\,d_o\,N_A}{1000}} \qquad (3)$$

where;

e: is the electronic charge

D: is the dielectric constant

k: is the Boltzmann's constant

T: is the absolute temperature

d_o: is the solvent density

N_A: is Avogadro's number

The Debye-Hückel [16] limiting law was tested and found to be in agreement with the Lewis-Randall empirical rule which states that the activity coefficient in dilute solution is the same as in solution of the same ionic strength. By more thorough tests, significant deviations from the limiting law expression were observed at ionic strength as low as molality of 0.01. The deviations were believed to be due to the assumptions and simplifications made in deriving the ionic atmosphere potential equation. Debye and Hückel [16] recognized this and tried to improve their law. For higher electrolyte concentration, the following empirical modification had been proposed:

$$\ln(\gamma_{\mp}) = \frac{-A * |Z_+ * Z_-|\sqrt{I}}{1 + Ba\sqrt{I}} \qquad (4)$$

where;

$$B = \sqrt{\frac{8\,\pi\,e^2\,d_o N_A}{1000\,D\,k\,T}}$$

a: is a constant related to the average hydrated radius of ions usually about 4 A°

The product B×a is sometimes set equal to unity or treated as an adjustable parameter. Equation. 3 was then known as the extended Debye-Hückel law which was then improved by adding a correction term to become:

$$\ln(\gamma_{\mp}) = \frac{-A|Z_+ Z_-|\sqrt{I}}{1 + Ba\sqrt{I}} + C\,I \qquad (5)$$

where C is an adjustable parameter and is sometimes set equal to $0.1|Z_+ Z_-|$.

Equations 3 and 4 are satisfactory for solutions of molality of 0.1. With best accuracy for 1:1 electrolyte and become progressively less accurate for 1:2, 2:2, *etc*... electrolytes. Equations1, 3 and 4 are valid for solutions of mixed electrolytes, as well as, single electrolytes. In the case of several electrolytes, there are several mean activity coefficients, one for each electrolyte, whose values are computed by summing over all ions in solution and is considered the same for each electrolyte in the solution.

However, most of the work of Partanen and his co-workers [18-26], have shown that following Hückel equations apply very well to the thermodynamic properties of aqueous solutions of many uni-univalent salts at least up to the molality of 1.

Another approach for calculating the activity coefficient of an ion or electrolyte in a mixture is the virial expansion of the activity coefficient.

Guggenheim [27] added constant virial coefficients which can be fitted empirically to the extended Debye-Hückel [16] limiting law in order to extend the application of the law to higher concentrations. The equation for the mean activity coefficient of an electrolyte of cation $\acute{M}$ and anion $\acute{X}$ is:

$$\ln(\gamma_{\acute{M}\acute{X}}) = \frac{-A*|Z_{\acute{M}}*Z_{\acute{X}}|\sqrt{I}}{1+\sqrt{I}} + \frac{2\,v_+}{v_+ + v_-}\sum_X \beta_{\acute{M}X}\, m_X + \frac{2\,v_-}{v_+ + v_-}\sum_X \beta_{M\acute{X}}\, m_M \tag{6}$$

where;

v_+ is the number of cations per molecules of electrolyte

v_- is the number of anions per molecules of electrolyte

The constant β_{MX} are constant coefficients at given T and D which represents the net effect of various short range forces between M and X ions. Guggenheim equation was quite successful for solutions of ionic strength of about a molality of 0.1.

The next step was to allow the virial coefficient to vary with ionic strength in order to account for higher concentrations. In this case the activity coefficient of an ion in a mixture is calculated using the following virial expression:

$$\ln(\gamma_i) = l\,n(\gamma_{DH}) + \sum_j B_{ij}(I) m_j + \sum_{jk} C_{ijk}(I)\, m_j\, m_k + \cdots \tag{7}$$

where;

γ_{DH} is the activity coefficient calculated by Debye-Hückel law.

$B_{ij}(I)$ and $C_{ijk}(I)$ are the second and third virial coefficients respectively which are ionic strength dependent.

Pitzer and co-workers supported this trend and investigated the functional form of the second virial coefficients while the term for the triple ion interactions was assumed to be independent of ionic strength. The basic equation for their model was the total excess Gibbs energy (G^{ex}) for a solution containing n_w kg of solvent and n_i, n_j, .. moles of solute species i, j, which is given by:

$$\frac{G^{ex}}{RT} = n_w\, f(I) + \frac{1}{n_w}\sum_{ij} \lambda_{ij}(I) n_i n_j + \frac{1}{{n_w}^2}\sum_{ijk} \mu_{ijk}(I)\, n_i\, n_j n_k + \cdots \tag{8}$$

where;

$f(I)$ is a function describing the long-range electrostatic effects as a function of temperature

$\lambda_{ij}(I)$ is a term describing the effect of short-range forces between species I and j as a function of ionic strength.

$\mu_{ijk}(I)$ is a term for triple ion interactions independent of ionic strength which may be significant at high concentrations.

The matrices λand μ are assumed symmetric, i.e. $\lambda_{ij} = \lambda_{ji}$

Their lengthy work led them to develop a system of equations for predicting the thermodynamic properties of electrolytes. They presented their work in a series of papers and the following is the system of Pitzer's equations for aqueous solutions at 25°C given the notation used by Krumgalz and Millero [28].

$$\ln(\gamma_M) = Z_M^2 f^\gamma + 2\sum_a m_a X_a + \sum_c \sum_a m_a m_c\, X_{ca} + \ldots \tag{9}$$

$$\ln(\gamma_x) = Z_x^2 f^\gamma + 2\sum_c m_c X_{ac} + \sum_c \sum_a m_a\, m_c X''_{ca} + \ldots \tag{10}$$

$$f^\gamma = -A^\phi \left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln(1+b\sqrt{I})\right] \tag{11}$$

$$X_a = B_{M\,a} + \frac{1}{2}(\sum_i m_i |Z_i| C_{M\,a} \tag{12}$$

$$X_c = B_{c\,x} + \frac{1}{2}(\sum_i m_i |Z_i| C_{c\,x} \tag{13}$$

$$X'_{c\,a} - Z_M^2 B'_{c\,a} + Z_M C_{c\,a} \tag{14}$$

$$X''_{c\,a} - Z_X^2 B'_{c\,a} + |Z_x| C_{c\,a} \tag{15}$$

$$C_{MX} = \frac{C^\Phi_{MX}}{(2|Z_M Z_X|^{0.5})} \tag{16}$$

For 1:1, 2:1, 3:1 and 4:1 electrolytes the terms $B_{M\,X}$ and $B'_{M\,X}$are given by:

$$B_{MX} = \beta^{(o)}_{M\,X} + (\frac{2\,\beta^{(1)}_{M\,X}}{\alpha_1^2 I})[1 - (1+\alpha_1 I^{0.5})\exp(-\alpha_1 I^{0.5})] \tag{17}$$

$$B'_{M\,X} = (\frac{2\,\beta^{(1)}_{M\,X}}{\alpha_1^2\, I^2})\left[-1 + \left(1 + \alpha_1 I^{0.5} + \frac{1}{2}\alpha_1^2\, I\right)\exp(-\alpha_1 I^{0.5})\right] \tag{18}$$

The subscripts M and C refer to cations, while X and A refer to anions. $\sum_a$ *and* $\sum_c$ indicate summation of the properties of all anions and cations, respectively. The parameter b is set equal to 1.2 and held constant for solutes and temperatures as indicated by Zemaitis [7]. For 1:1, 2:1, 3:1, 4.1 and 5:1 electrolytes α = 2 and considered to be temperature independent. The interaction parameters $\beta^{(o)}_{M\,X}$, $\beta^{(1)}_{M\,X}$ and $C^\phi_{MX}$are given by Pitzer and Mayorga [10]. Table 1 presents the value of these parameters for the salt found in the commercial potash produced by APC.

In this system of equations β's and C's represent measurable combinations of the second and third virial coefficients, respectively, and they are parameterized from single salt systems. The main contribution to $\beta^{(1)}_{MX}$ come from the short-range interactions of unlike charged ions, and the short-range interaction of both unlike and like charged ions contribute to $\beta^{(0)}_{MX}$, while C^{ϕ}_{MX} relates to triple interactions [28]. Also, in this system of equations, both mixed electrolyte second virial coefficients (φ's) and third virial coefficients (ψ's) which account for the interactions between ions of like sign are ignored since they contribute little or nothing to the calculations as was mentioned by Zemaitis [7].

Silvester and Pitzer [12] suggested methods for adapting the model and the parameters to any temperature. Most of their work was to investigate the effect of temperature on $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$ and C^{ϕ}_{MX} for NaCl in the temperature range (25-300°C). They noted that the parameters were slightly affected by temperature while the Debey-Hückel parameter A^{ϕ} was much more affected due to the decrease in the dielectric constant. The values obtained for A^{ϕ} are listed in Table 2.

The temperature derivatives of $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$ and C^{ϕ}_{MX} for various species are given in Zemaitis[7] and they are listed in Table 3. They can be used to convert the values of these parameters, which are given at 25°C (Table 1), to other temperatures provided the temperature change is not too high. The parameters b and α_1 are temperature independent as stated before.

3. Material and Methods

Apparatus

A simple apparatus was used to determine the solubility of potash produced by APC. This apparatus consisted of a stopped flask of 250cm^3 capacity immersed in a thermostatically controlled water bath (Ultratemp 2000 Julabo f 30, -50°C -200°C, accuracy of 0.05°C). The flask was fitted with a stirrer to agitate the content of the flask during the experiment.

Experimental Method

The flask was filled with 100cm^3 of distilled water and a suitable amount of potash was added. The flask was then closed by a stopper and immersed in the water bath whose temperature was set at the desired value. The stirrer was switched on and the whole set was allowed to stand for an hour, still at constant temperature to enable any finely dispersed solids to settle. A sample of the clear liquid was carefully withdrawn by means of a warmed pipette and a weighed quantity of the sample was analyzed for K^+, Na^+, Mg^{++} and Ca^{++} using a pye Unicam Sp8 atomic absorption spectrophotometer. The chloride ion concentration was calculated from positive charge balance assuming that the chloride is the only anion that existed in the sample. The experiment was repeated at eight different temperatures (25, 30, 35, 40, 45, 50, 60 and 70°C).

4. Results and Discussion

Since the commercial potash used in this study is about 97% KCl, the other salts (NaCl, $MgCl_2$, $CaCl_2$) will be considered as trace compounds. Therefore, the saturation reaction and the solubility equilibrium constant are written as follows:

$$(KCl)_s \leftrightarrows (K^+ + Cl^-)_{aq}$$

$$K_{sp} = a_{K^+} * a_{Cl^-} \quad (19)$$

$$K_{sp} = (\gamma_{K^+} m_{K^+}) * (\gamma_{Cl^-} m_{Cl^-}) = \gamma^2_{KCl}(m_{K^+}\, m_{Cl^-}) \quad (20)$$

$$\log K_{sp} = 2\,\log \gamma_{KCl} + 2\,\log m_{K^+} \quad (21)$$

The molalities and the activity coefficients of different ions which are calculated by Pitzer's model are listed in Table 4 at different temperatures.

If one molecule of an electrolyte dissociates into ν ions of which ν_+ are cations and ν_- are anions, then the mean activity coefficient of the electrolyte, $\gamma_\mp$, is related to the individual ionic activity coefficients γ_+ and γ_- by:

$$\gamma_\mp = (\gamma_+^{\nu_+}\gamma_-^{\nu_-}) \quad (22)$$

Using this equation and the measured saturation molalities of KCl salt, the equilibrium solubility constants are calculated at different temperatures. These values are listed in Table 5 together with the values calculated by Wood [5,6].

The equilibrium solubility constant was correlated to the temperature through the following correlation:

$$K_{sp} = 0.3505\ T(\,^oC) \quad (23)$$

Table 5 shows that the deviations between the equilibrium solubility constant calculated in this study and those calculated by Wood's model increase as the temperature (concentration) increases. These deviations could be attributed to the absence of a third virial coefficient in Wood's model. This absence might lead to lower the estimation of the activity coefficient and hence to lower estimation of the equilibrium constant. Pitzer and co-workers [9,10] indicated that third and even higher virial coefficients must be included to predict more accurate thermodynamic properties above ionic strength of 4 molal. Other reasons are believed to be due to experimental error committed during the measurement of solubility. This error is due to the interference of trace ions present in the solution (Na^+, Mg^{++}, Ca^{++}) which affects measuring the concentration of K^+ ion by the atomic absorption spectrophotometer. This interference could lead to overestimation of K^+ ion concentration as it was found to be 4.95 M at 25°C while the published value is 4.81M when using pure KCl salt. Therefore, it is recommended to use probes of high selectivity to measure different ion concentrations. The increase of deviation with temperature suggests that the temperature-dependent parameters need more refinement in both models so that closer values could be obtained.

Table 1: Values of $\beta^{(o)}_{MX}$, $\beta^{(1)}_{MX}$ and C^{ϕ}_{MX} at 25°C

Salt	$\beta^{(o)}_{MX,}$	$\beta^{(1)}_{MX}$	C^{ϕ}_{MX}
KCl	0.04835	0.2122	-0.00084
NaCl	0.0765	0.2664	0.00127
$MgCl_2$	0.35235	1.6815	0.00519
$CaCl_2$	0.3159	1.6140	-0.00034

Table 2. The Debey-Hückel parameter A^{Φ} for the asmotic function at various temperature.

T (°C)	0	10	20	25	30	40	50	60	70	80	90	100
A^{Φ}	0.3770	0.382	0.3878	0.391	0.3944	0.4017	0.4098	0.4185	0.4270	0.438	0.4488	0.4603

Table 3. Temperature derivatives of the parameter $\beta^{(o)}_{MX}$, $\beta^{(1)}_{MX}$ and C^{ϕ}_{MX} for different salt.

Salt	$(\frac{\partial \beta^{(o)}}{\partial T})_P$	$(\frac{\partial \beta^{(1)}}{\partial T})_P$	$(\frac{\partial C^{\phi}}{\partial T})_P$
KCl	5.794×10^{-4}	10.71×10^{-4}	-5.095×10^{-5}
NaCl	5.175×10^{-4}	7.005×10^{-4}	-10.54×10^{-5}
$MgCl_2$	$-0.23 \times 3/4 \times 10^{-3}$	$5.2 \times 3/4 \times 10^{-3}$	-
$CaCl_2$	$-0.572 \times 3/4 \times 10^{-3}$	$4.87 \times 3/4 \times 10^{-3}$	-

Table 4. Molalities and activity coefficients at different temperatures.

T (°C)	m_{K+}	m_{Na+}	m_{Ca++}	m_{Mg++}	m_{cl-}	γ_{K+}	γ_{Na+}	γ_{Ca++}	γ_{Mg++}	γ_{cl-}
25	4.95712	0.204814	0.001844	0.0301	5.2257	0.5923	0.886	1.0051	1.7486	0.6165
30	5.2465	0.225939	0.001881	0.032423	5.5427	0.6082	0.9308	1.1114	1.9761	0.6346
35	5.5043	0.245491	0.0019126	0.034527	5.8258	0.6178	0.9639	1.1576	2.0935	0.6459
40	5.57379	0.26379	0.0019406	0.036459	6.0826	0.6362	1.0097	1.2615	2.3117	0.6664
45	5.9521	0.281059	0.0019655	0.038253	6.3186	0.6447	1.0374	1.2716	2.3534	0.6764
50	6.1505	0.297464	0.0019882	0.039932	6.5374	0.6638	1.081	1.3574	2.5302	0.6974
60	6.5096	0.328145	0.0020279	0.043015	6.9341	0.6896	1.1440	1.4019	2.6330	0.7263
70	6.8294	0.38541	0.0020622	0.045805	7.2882	0.7135	1.1977	1.3980	2.6259	0.7528

Table 5. The measured saturation molalities of KCl salt and the equilibrium solubility constants

T (°C)	$m_{salt, K+}$ present work	Log (K_{sp}) present work	Log K_{sp} (Wood) (Reference)	% deviation
25	4.95712	0.95296	0.894	6.6
30	5.2465	1.02634	0.9379	9.4
35	5.5043	1.04391	-	-
40	5.7379	1.14480	1.0238	12
45	5.9521	1.18895	-	-
50	6.1505	1.24335	1.0988	13
60	6.5096	1.32681	1.1615	14
70	6.8294	1.39885	1.2163	15

5. Conclusion

The Pitzer's model was easily adapted to calculate the activity coefficients of commercial potash at temperatures in the range of (25-70^oC). The equilibrium solubility constants of potash in this temperature range were calculated using these activity coefficients and it was found that the equilibrium constant could be correlated to temperature by the correlation $K_{sp} = 0.3505\, T(^oC)$. The calculated equilibrium constants were compared to the values obtained by Wood for pure potash. Good agreement was obtained at low temperatures (below 40^oC) and more deviation was observed at higher temperatures.

Nomenclature

A	is the Debye-Hückel constant
A^{Φ}	Debey-Hückel parameter for osmotic coefficient
a	is a constant related to the average hydrated radius of ions usually about 4 A^o
B_{ij}, λ_{ij}	Second virial coefficient
b	Parameter usually set equal to 1.2
μ_{ijk}, C_{ijk}	Third virial coefficient
D	Dielectric constant
d_o	Solvent density
e	Electronic charge
G^{ex}	Total excess Gibbs energy
I	Ionic strength in molality scale
K_{sp}	Solubility equilibrium constant
k	Boltzmann's constant
m	molality
N_A	Avogadro's number
n_w	Amount of solvent in kg
n_i	Moles of solute species
R	Universal gas constant
T	Temperature
Z	Number of charge
A	Parameter usually set equal to 2
γ	Activity coefficient
v_+	Number of cations per molecules of electrolyte
v_-	Number of anions per molecules of electrolyte
Y	$(= v_+ + v_-)$

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