# Effect of temperatures on potassium adsorption in saline soils within Nineveh Governorate, Iraq

## Abstract

Thermodynamic criteria were used to evaluate the behavior and available of potassium in saline soils. The study was conducted on three sites that differ in salt content in Nineveh Governorate - Iraq, and each site is divided into two depths (surface and subsurface). The study was conducted at three temperatures (278, 298, 318 Kelvin). The results of the study showed that there was an increase in the amount of potassium adsorbed and the percentage of adsorption with an increase in the amount of potassium added to the soil and for all samples of the study, and with regard to the ability of the soil to adsorption, the results showed a sudden increase in the adsorption of potassium at a high addition percentage to the level of added potassium, especially at levels (1 and 2). ) mmol.l$^{-1}$ for all study soils,the highest value of the ionic activity of potassium $AR_K$ in the study soil was at a temperature of 298 K, reaching ($14.05 \times 10^{-3}$) mol.l$^{-1/2}$ at the subsurface depth of the first site, and the lowest value reached ($1.61 \times 10^{-3}$). mol.l$^{-1/2}$ in the same sample at a temperature of 278 K, the values of free energy of potassium, $\Delta G_K$, in the studied soils ranged from the highest value, reaching ($-14.85\times10^{-3}$ kJ) at a temperature of 278 K, to the lowest value ($-10.56\times10^{-3}$ kJ) at a temperature of 298 K, in the subsurface depth of the first site. Regarding the values of entropy reaction, it ranged from the highest value -53.43 expressed in joule.mol$^{-1}$ in the subsurface depth of the first site at a temperature of 278 K to the lowest value of -35.46 in the same sample at a temperature of 298 K. Enthalpy values for the study samples were negative values, which indicates that the reaction is of the exothermic type, it was found that the highest negative value for enthalpy at a temperature of 278 K reached -29.70, expressed in kilojoule.mol$^{-1}$, at the subsurface depth of the first site, the lowest negative value is -20.42 in the same sample at a temperature of 298 K.

**Keywords**: ionic activity of potassium, free energy of potassium, entropy of potassium reaction, enthalpy of potassium

## Introduction

The process of potassium adsorption into the soil system is a chemical process that affects the available content of potassium. This process depends on the state of balance between the potassium present in the soil solution and the potassium that is located between the inner layers of minerals. The stabilized potassium constitutes 5-10 % of the total potassium content in Soil (Bayraktar, 2019). Mouhamed et al. (2016) indicated that the potassium adsorption process is affected by several factors, including soil aeration, soil moisture content, soil temperature, and quality of the prevailing clay minerals, and that the amount of available potassium constitutes approximately 1-2 % of the total amount of potassium in the soil. Soil temperature has a role in the available and movement of potassium in the soil system, as well as its role in the process of its absorption by the plant. In general, the speed of any chemical reaction increases with increasing temperatures whenever the temperature increases by 10 degrees Celsius. Al-Obaidi and Al-Zubaidi (2005) see the necessity of studying potassium reactions under the influence of different temperatures, especially in Iraqi environmental conditions, due to the large temperature fluctuations during the seasons of the year and during the day and night in a single day, in their study on the adsorption of potassium in calcareous soil from northern Iraq at three absolute temperatures ($278^{\circ}$, $298^{\circ}$, $318^{\circ}$ kelvin) using mixed displacement techniques, they found that there is a highly significant effect of temperature on the potassium adsorption and release reactions and the state of equilibrium between them. Al-Obaidi et al. (2010) explained that the release of potassium in the soil results from the decomposition of potassium-bearing minerals and an exchange reaction, which is very slow, potassium in the soil solution is constantly renewed by being released from the exchanged form and prepared from the non-exchanged form. As for Iraqi soils, as is the case in most soils in arid and semi-arid regions, they have a high reserve of potassium, but the speed of its release is slow and is not sufficient to meet the need of agricultural crops for this element (Al-Samarrai, 2005). The process of releasing potassium is an endothermic reaction, while the process of adsorption of potassium is an exothermic reaction. High soil temperature has a significant impact on the ability of minerals to fix potassium, which affects its available for plants (Al-Shibini, 2007), and Najafi-Ghiri et al. (2020) indicated that high temperature in calcareous soil leads to an increase in the amount of soluble potassium and exchangeable potassium, thus increasing the rate of potassium release. The ability to release potassium from the soil may be limited due to the change in the structure of potassium-bearing soil minerals and the decrease in the diffusion of potassium ions in the interlayer spaces of the minerals. The use of thermodynamic criteria in evaluating soil fertility to express potassium status and behavior in the soil helps in revealing an appropriate management method for each soil (Isnaini and Rivaie, 2023, Rani et al., 2023).

## Methods and Materials

1- Choosing study sites:

The study included three sites in the Rabia area within Nineveh Governorate - Iraq, for saline soils with different salinity levels. Soil samples were collected from the surface depth (0 - 25 cm) and the subsurface depth (25 - 50 cm) to conduct routine analyses. The soil samples were air-dried and ground using a wooden hammer, then sieved with a 2 mm sieve, and the amount of the three separations - clay, silt, sand, total calcium carbonate, organic matter, exchange capacity of positive ions, pH, and electrical conductivity (EC) - were estimated using the methods described (Carter and Gregorich, 2008). As shown in Table (1).

Table (1): some of chemical and physical properties for the studied soils.

| Depth | pH | EC | $CaCO_3$ | O.M | CEC | Soil Separates ($gm.kg^{-1}$) | | | Texture |
|---|---|---|---|---|---|---|---|---|---|
| | | $dS.m^{-1}$ | $gm.kg^{-1}$ | | $Cmol.kg^{-1}$ | Sand | Silt | Clay | |
| First Site | | | | | | | | | |
| Surface | 7.3 | 2.70 | 225 | 15.98 | 29.56 | 15.05 | 54.25 | 30.70 | SCL |
| Sub Surface | 7.4 | 5.10 | 220 | 18.36 | 32.17 | 9.70 | 44.50 | 45.80 | SC |
| Second Site | | | | | | | | | |
| Surface | 7.2 | 3.00 | 220 | 11.90 | 29.56 | 34.70 | 34.50 | 30.80 | CL |
| Sub Surface | 7.3 | 6.00 | 190 | 12.24 | 29.56 | 31.40 | 38.50 | 30.10 | CL |
| Third Site | | | | | | | | | |
| Surface | 7.4 | 7.80 | 195 | 15.98 | 26.95 | 16.50 | 31.00 | 52.50 | C |
| Sub Surface | 7.6 | 7.80 | 225 | 13.94 | 26.08 | 11.50 | 33.50 | 55.00 | C |

SCL: Silt Clay Loam, SC: Silt Clay, CL: Clay Loam, C: Clay

2- Potassium adsorption according to the concept of thermodynamics

Transparent plastic cans of 100 ml with a tight seal were used to study this adsorption. The cans were prepared with the number of concentrations of potassium prepared from potassium chloride (KCl) added as follows (0, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2) $mmol.l^{-1}$, 2.5 grams of study soil was placed in each box, and it was added these concentrations are in the form of volume and the volume is supplemented to 50 ml with 0.01 M $CaCl_2$ solution, after that, the plastic cans were shaken with a shaker for two hours and left to equilibrate for 48 hours at three temperatures (278°, 298°, 318° Kelvin), then the suspension in the cans was filtered to obtain the equilibrium solution in which potassium, calcium, magnesium, pH, and EC were determined. The amount of potassium adsorbed on the surface of the solid phase, K - quantity, was calculated, as well as the intensity of potassium in the equilibrium solution, K - intensity, which is expressed as the relative effectiveness of potassium in the equilibrium solution according to the ratio law, as mentioned by (Beckett, 1964), and it was calculated from the following equation:

$$AR_K = \frac{a\,K}{a\,Ca + a\,Mg}$$

$AR_K$: relative effectiveness of potassium

The mathematical relationship was drawn between the amount of potassium adsorbed, expressed by ($\pm\Delta K$), which represents potassium in the solid soil phase (Q) quantity on the y-axis, and the intensity of potassium in the liquid soil phase (I) intensity on the x-axis, which is ($AR_K$), and through this Relationship, the following constants can be found for potassium:

1. Potassium effectiveness ratios at equilibrium ($AR_K$): it represents the intersection of Q/I with the x-axis

2. free energy $\Delta G$: it can be calculated from the equation proposed by (Woodruff, 1955) : $-\Delta G = 2.303\ RT \log AR_K$

3. amount of potassium adsorbed on the exchange surface was calculated from the following relationship***:*** $K.ad = (K_{in} - K_{fin}) \times V/S$

K.ad: adsorbed amount, $K_{in}$ : added-K , $K_{fin}$: balanced-K, V: volume of solution, S: soil mass.

4. adsorbed potassium was calculated from the following relationship:

adsorbed-K = ($K_{in} - K_{fin}$)

5. percentage of adsorption or release was calculated from the following relationship :
% adsorbed or release = (adsorbed-K / Added-K) * 100

6. Entropy was calculated by dividing free energy by temperature

## Results and Discussion

### 1- Effect of the added potassium level on potassium adsorption:

In order to know the behavior of ion exchange of potassium in the soil of the study, the adsorption of potassium was studied, which is one of the most important chemical reactions that occur between the liquid phase and the solid phase of the soil. Through it, potassium is transferred mutually with other ions between the two phases and ends after a certain period of time when a dynamic equilibrium of the ions exchanged between the two phases occurs. Adsorption is also affected by the surface area of the mineral colloids, dissolution, temperature, reaction degree pH, and salinity (Moharami and Jalali , 2013), as Ogwada and Sparks (1986) see, potassium added to the soil binds to the surface of the solid phase of the colloidal fraction in a stabilizing manner that depends on two main mechanisms:

first mechanism: involves stabilizing potassium between the layers of crystals in three-layer minerals (1:2). This type of stabilization is accompanied by the transformation of vermiculite into a mica mineral. formation of these minerals can be confirmed through the use of X-ray diffraction (XRD) and the plane (001), where the crystal dimension shrinks from (15 Å to 12.5 Å and to 10 Å). Such changes may cause a decrease in the exchange capacity of positive ions.

second mechanism: in which potassium is stabilized through the formation of insoluble potassium compounds such as aluminosilicates, and high pH values accelerate the formation of these components.

Tables (2, 3, and 4) show the amounts of potassium adsorbed, which varied according to the level of added potassium and according to the soil properties that have a direct relationship with adsorption. In general, there was an increase in the amount of potassium adsorbed and the percentage of adsorption with an increase in the amount of potassium added to the soil and for all soils of the study, the reason for this is that the specialized adsorption sites were occupied by the added potassium, which could occur at the beginning of the reaction, and in the subsequent stages. Saturation of non-specialized sites, so any amount of potassium added to the soil is offset by an increase in the amount of potassium in the equilibrium solution (Thajeel, 2013).

Table (2): Quantities of added and adsorbed potassium and the rate of adsorption or release to the first site at different temperatures

| K Added | Depth | K equilibrium | K adsorbed | Adsorb/ Release | Depth | K equilibrium | K adsorbed | Adsorb/ Release |
|---|---|---|---|---|---|---|---|---|
| mmol.l$^{-1}$ | | mmol.l$^{-1}$ | mmol.l$^{-1}$ | % | | mmol.l$^{-1}$ | mmol.l$^{-1}$ | % |
| at 278° Kelvin | | | | | | | | |
| 0 | Surface | 0.12 | -0.12 | -- | Sub Surface | 0.10 | -0.1 | -- |
| 0.1 | | 0.15 | -0.05 | -500.0 | | 0.12 | -0.02 | -20.0 |
| 0.2 | | 0.17 | 0.03 | 15.0 | | 0.17 | 0.03 | 15.0 |
| 0.4 | | 0.23 | 0.17 | 42.5 | | 0.23 | 0.17 | 42.5 |
| 0.6 | | 0.30 | 0.3 | 50.0 | | 0.28 | 0.32 | 53.3 |
| 0.8 | | 0.35 | 0.45 | 56.2 | | 0.35 | 0.45 | 56.2 |
| 1 | | 0.43 | 0.57 | 57.0 | | 0.43 | 0.57 | 57.0 |
| 2 | | 0.76 | 1.24 | 62.0 | | 0.76 | 1.24 | 62.0 |
| at 298° Kelvin | | | | | | | | |
| 0 | Surface | 0.30 | -0.3 | -- | Sub Surface | 0.30 | -0.3 | -- |
| 0.1 | | 0.35 | -0.25 | -250.0 | | 0.35 | -0.25 | -250.0 |
| 0.2 | | 0.40 | -0.2 | -100.0 | | 0.43 | -0.23 | -115.0 |
| 0.4 | | 0.53 | -0.13 | -32.5 | | 0.56 | -0.16 | -40 |
| 0.6 | | 0.66 | -0.06 | -10 | | 0.71 | -0.11 | -18.33 |
| 0.8 | | 0.81 | -0.01 | -1.25 | | 0.84 | -0.04 | -5.0 |
| 1 | | 0.97 | 0.03 | 3.0 | | 0.97 | 0.03 | 3.0 |
| 2 | | 1.79 | 0.21 | 10.5 | | 1.84 | 0.16 | 8.0 |
| at 318° Kelvin | | | | | | | | |
| 0 | Surface | 0.30 | -0.3 | -- | Sub Surface | 0.28 | -0.28 | -- |
| 0.1 | | 0.40 | -0.3 | -300.0 | | 0.40 | -0.3 | -300.0 |
| 0.2 | | 0.43 | -0.23 | -115.0 | | 0.43 | -0.23 | -115.0 |
| 0.4 | | 053 | -0.13 | -32.5 | | 0.56 | -0.16 | -40.0 |
| 0.6 | | 0.66 | -0.06 | -10.0 | | 0.69 | -0.09 | -15.0 |
| 0.8 | | 0.79 | 0.01 | 1.25 | | 0.79 | 0.01 | 1.25 |
| 1 | | 0.89 | 0.11 | 11.0 | | 0.86 | 0.14 | 14.0 |
| 2 | | 1.57 | 0.43 | 21.5 | | 1.66 | 0.34 | 17.0 |

(+): adsorption (-): release

We also note from the same tables that the amount of potassium adsorbed and the percentage of adsorption differed from one soil to another for the soils of the study, and the reason for this variation is that potassium is affected by the processes of adsorption and sedimentation, as well as the exchange capacity of positive ions, the degree of soil reaction, the amount of calcium carbonate and organic matter, and the type and content of clay and clay minerals, potassium content and the chemical composition of the soil solution (Al-Qattan, 2023). The results that we obtained included a sudden increase in potassium adsorption at a high addition rate for the added potassium level, especially at the level of (1 and 2) mmol.L$^{-1}$ for all study soils, the reason for this is due to the possibility of the complete transformation of the smectite mineral into octahedral and the occurrence of a Rotation phenomenon of the hydroxyl group OH, which leads to a sudden increase in stabilization (Sparks, 2022).

Table (3): Quantities of added and adsorbed potassium and the rate of adsorption or release to the second site at different temperatures

| K Added | Depth | K equilibrium | K adsorbed | Adsorb/ Release | Depth | K equilibrium | K adsorbed | Adsorb/ Release |
|---|---|---|---|---|---|---|---|---|
| mmol.l$^{-1}$ | | mmol.l$^{-1}$ | mmol.l$^{-1}$ | % | | mmol.l$^{-1}$ | mmol.l$^{-1}$ | % |
| at 278° Kelvin | | | | | | | | |
| 0 | Surface | 0.30 | -0.3 | -- | Sub Surface | 0.12 | -0.12 | -- |
| 0.1 | | 0.38 | -0.28 | -280.0 | | 0.17 | -0.07 | -70.0 |
| 0.2 | | 0.43 | -0.23 | -115.0 | | 0.23 | -0.03 | -150.0 |
| 0.4 | | 0.51 | -0.11 | -27.5 | | 0.30 | 0.10 | 25.0 |
| 0.6 | | 0.63 | -0.03 | -5.0 | | 0.43 | 0.17 | 28.3 |
| 0.8 | | 0.69 | 0.11 | 13.7 | | 0.51 | 0.29 | 36.2 |
| 1 | | 0.81 | 0.19 | 19.0 | | 0.51 | 0.49 | 49.0 |
| 2 | | 1.40 | 0.60 | 30.0 | | 0.86 | 1.14 | 57.0 |
| at 298° Kelvin | | | | | | | | |
| 0 | Surface | 0.35 | -0.35 | -- | Sub Surface | 0.20 | -0.2 | -- |
| 0.1 | | 0.43 | -0.33 | -330.0 | | 0.25 | -0.15 | -150.0 |
| 0.2 | | 0.56 | -0.36 | -180.0 | | 0.30 | -0.1 | -50.0 |
| 0.4 | | 0.63 | -0.23 | -57.5 | | 0.38 | 0.02 | 5.0 |
| 0.6 | | 0.79 | -0.19 | -31.6 | | 0.58 | 0.02 | 3.3 |
| 0.8 | | 0.92 | -0.12 | -15.0 | | 0.66 | 0.14 | 17.5 |
| 1 | | 1.04 | -0.04 | -4.0 | | 0.74 | 0.26 | 26.0 |
| 2 | | 1.79 | 0.21 | 10.5 | | 1.30 | 0.7 | 35.0 |
| at 318° Kelvin | | | | | | | | |
| 0 | Surface | 0.38 | -0.38 | -- | Sub Surface | 0.20 | -0.2 | -- |
| 0.1 | | 0.46 | -0.36 | -360.0 | | 0.28 | -0.18 | -180.0 |
| 0.2 | | 0.48 | -0.28 | -140.0 | | 0.33 | -0.13 | -65.0 |
| 0.4 | | 0.58 | -0.18 | -45.0 | | 0.40 | 0 | 0.0 |
| 0.6 | | 0.71 | -0.11 | -18.3 | | 0.51 | 0.09 | 15.0 |
| 0.8 | | 0.81 | -0.01 | -1.2 | | 0.61 | 0.19 | 23.7 |
| 1 | | 0.89 | 0.11 | 11.0 | | 0.63 | 0.37 | 37.0 |
| 2 | | 1.54 | 0.46 | 23.0 | | 1.27 | 0.73 | 36.5 |

(+): adsorption (-): release

There are also three specialized sites on the surfaces of some minerals, including illite, in which the potassium binding strength varies: the surfaces, the edges, and between the layers, which makes the speed of potassium release and adsorption vary. The total charge density and its distribution between the octahedral and tetrahedral sheets greatly affects the presence of the potassium ion in the group minerals (2:1) (Schneider et al, 2005). In this regard, some minerals have the ability to re-fix the added potassium in non-exchangeable forms. Therefore, the process of releasing potassium from these minerals into forms that are soluble, exchangeable, and adsorption are reversible equilibrium reactions controlled by the energy of binding potassium to the exchange surfaces or its presence within the interstitial spaces of the layers clay minerals 2:1 as described by (Bhonsle et al., 1992). Accordingly, we find that potassium that is released quickly is bound to the exchange surfaces (clay surfaces) and is controlled by the Vanderwaals bond, while potassium that is released slowly is bound to sites within the structural structure of the mineral, and its release from those sites requires more energy (Sparks, 2017).

## 2- ability of soil to absorb potassium at different temperature:

The results shown in tables (2, 3, and 4) indicate that the amount of potassium fixed in the study soil samples at the different levels of added potassium was characterized by the release of amounts of potassium to varying degrees between the soils and the different temperatures. In the study soil samples, adsorption appeared at the third and fourth addition levels ( 0.2 and 0.4 mmol.l$^{-1}$) at a temperature of 278°K for both depths, except for the soil of the superficial depth of the second site, which was adsorption appeared at the sixth level of addition (0.8 mmol.l$^{-1}$). While at a temperature of 298°K, adsorption appeared at the seventh and eighth addition levels (1 and 2 mmol.l$^{-1}$) and for both depths, except for the soil at the subsurface depth of the second site and both depths of the third site, where adsorption appeared at the fourth addition level (0.4 mmol.l$^{-1}$), but at the high temperature of 318°K, potassium adsorption appeared at the seventh and eighth addition levels (1 and 2 mmol.l$^{-1}$) for all soils at the superficial depth. As for the subsurface depth, adsorption appeared at the fifth and sixth addition levels (0.6 and 0.8 mmol.l$^{-1}$). In general, we noticed a decrease in the ability of the study soil to absorb potassium at a temperature of 298°K, which represents the spring and fall temperature, and it is the best temperature at which larger amounts of potassium are released compared to the summer temperature (318°K) and the winter temperature (278°K). The reason for this may be due to rapid saturation of the specialized and non-specialized sites for potassium adsorption, which can occur in the first hours of the equilibrium period and thus occupies the space of most adsorption sites in the soil and their percentage decreases. Thus, any increase in added potassium will reduce the potassium present in the equilibrium solution and thus its spread to within the crystalline structure of clay minerals. Also, the variation in stabilization behavior with the increase of potassium added to the soil and the difference in its ability to adsorption and release clearly reflects the role of the chemical, mineral and physical properties of these soils, and as Al-Jubouri (2017) showed that there are several processes involved in the processes of release and adsorption of potassium from the soil, including those related to mineral and organic components in the soil. Since the Iraqi soil is dominated by conditions of drought and salt accumulation, and is rich in minerals containing potassium, it has a decent store of this element, but with a low speed of release depending on the mineral composition of the soil, especially the quality of surface-active clay minerals that are not only important in the processes of fixation and release of potassium, but they also affect the freedom and movement of potassium in the soil through the adsorption of potassium ions on adsorption sites that differ in the extent her preference. Li et al.

(2022) and Das et al. (2019) showed that the ability of soil to adsorb and release ions, including potassium, depends on the structural structure of the clay minerals due to the element atoms they contain within the layers of the mineral (the tetrahedral and octahedral layers). For example, it leads The presence of potassium-bearing minerals such as mica and illite significantly increases the concentration of potassium in the soil solution.

Table (4): Quantities of added and adsorbed potassium and the rate of adsorption or release to the third site at different temperatures

| K Added | Depth | K equilibrium | K adsorbed | Adsorb/ Release | Depth | K equilibrium | K adsorbed | Adsorb/ Release |
|---|---|---|---|---|---|---|---|---|
| mmol.l$^{-1}$ | | mmol.l$^{-1}$ | mmol.l$^{-1}$ | % | | mmol.l$^{-1}$ | mmol.l$^{-1}$ | % |
| at 278° Kelvin | | | | | | | | |
| 0 | Surface | 0.20 | -0.2 | -- | Sub Surface | 0.17 | -0.17 | -- |
| 0.1 | | 0.23 | -0.13 | -130.0 | | 0.20 | -0.1 | -100.0 |
| 0.2 | | 0.28 | -0.08 | -40.0 | | 0.25 | -0.05 | -25.0 |
| 0.4 | | 0.35 | 0.05 | 12.5 | | 0.30 | 0.1 | 25.0 |
| 0.6 | | 0.40 | 0.2 | 33.3 | | 0.38 | 0.22 | 36.6 |
| 0.8 | | 0.51 | 0.29 | 36.2 | | 0.73 | 0.07 | 8.7 |
| 1 | | 0.56 | 0.44 | 44.0 | | 0.92 | 0.08 | 8.0 |
| 2 | | 1.38 | 0.62 | 31.0 | | 1.66 | 0.34 | 17.0 |
| at 298° Kelvin | | | | | | | | |
| 0 | Surface | 0.28 | -0.28 | -- | Sub Surface | 0.23 | -0.23 | -- |
| 0.1 | | 0.33 | -0.23 | -230.0 | | 0.28 | -0.18 | -180.0 |
| 0.2 | | 0.35 | -0.15 | 75.0 | | 0.30 | -0.1 | -50.0 |
| 0.4 | | 0.40 | 0 | 0.0 | | 0.35 | 0.05 | 12.5 |
| 0.6 | | 0.51 | 0.09 | 15.0 | | 0.46 | 0.14 | 23.3 |
| 0.8 | | 0.56 | 0.24 | 30.0 | | 0.56 | 0.24 | 30.0 |
| 1 | | 0.63 | 0.37 | 37.0 | | 0.63 | 0.37 | 37.0 |
| 2 | | 1.27 | 0.73 | 36.5 | | 1.30 | 0.7 | 35.0 |
| at 318° Kelvin | | | | | | | | |
| 0 | Surface | 0.33 | -0.33 | -- | Sub Surface | 0.28 | -0.28 | -- |
| 0.1 | | 0.38 | -0.28 | -280.0 | | 0.30 | -0.2 | -200 |
| 0.2 | | 0.43 | -0.23 | -115.0 | | 0.35 | -0.15 | -75.0 |
| 0.4 | | 0.48 | -0.08 | -20.0 | | 0.43 | -0.03 | -7.5 |
| 0.6 | | 0.53 | 0.07 | 11.6 | | 0.51 | 0.09 | 15.0 |
| 0.8 | | 0.63 | 0.17 | 21.2 | | 0.58 | 0.22 | 27.5 |
| 1 | | 0.71 | 0.29 | 29.0 | | 0.69 | 0.31 | 31.0 |
| 2 | | 1.22 | 0.78 | 39.0 | | 1.15 | 0.85 | 42.5 |

(+): adsorption (-): release

### 3- Effect of temperature on the ionic activity ratios of potassium at equilibrium ($AR^0_K$)

Ionic activity has been used in research to evaluate the available of some nutrients, including potassium, and for the purpose of identifying locations where adsorption occurs on the surfaces of the solid phase of soil, we have relied on relative effectiveness values. The values of the relative effectiveness of potassium, $AR^0_K$, represent the intensity of potassium in the solid phase of the soil when there is no loss or gain of potassium in the soil system. They are a measure of the instantaneous available content of the soil and have no relationship to the soils ability to release or prepare the ion over a long period of time (Wakeel and Ishfaq, 2022). The lowest value of ionic activity was recorded at the subsurface depth of the first site ($1.61846\times10^{-3}$) $mol.l^{-1/2}$, while the highest value of ionic activity rates at the surface depth of the second site was ($6.270\times10^{-3}$) $mol.l^{-1/2}$, at a temperature of 278° K and a rate of ($3.20\times10^{-3}$) $mol.l^{-1/2}$, when the equilibrium temperature was increased to 298° K, it led to a high increase in the ionic activity values. We noticed that the lowest value was at the subsurface depth of the third site ($3.96\times10^{-3}$) $mol.l^{-1/2}$, and the highest value appeared at the surface depth of the site. The first is ($14.0517\times10^{-3}$) $mol.l^{-1/2}$, with a rate of ($8.63\times10^{-3}$) $mol.l^{-1/2}$. As for the temperature of 318° K, we noticed that the lowest values were in the subsurface depth of the fourth site ($3.6787\times10^{-3}$) $mol.l^{-1/2}$, and the highest values were ($10.2284\times10^{-3}$) $mol.l^{-1/2}$, at the surface depth of the first site, at a rate of ($7.37\times10^{-3}$) $mol.l^{-1/2}$ (table 5). These values indicate that adsorption occurs in locations between layers of minerals as well as at the edges, as indicated by Hamed (2017) that values that are more than ($1\times10^{-2}$) $mol.l^{-1/2}$ indicate the dominance of adsorption over (Positions). Planner), while values less than ($1\times10^{-2}$) $mol.l^{-1/2}$ indicate the dominance of adsorption (edge site). This confirms that the adsorption process is accompanied by stabilization processes that are slow and occur between layers of minerals clay is the result of rapprochement between ions and the exchange surface in soils (Bilias and Barbayiannis, 2019). We note that a rise in temperature above 278° K generally led to a clear increase in the relative effectiveness values, this effect of temperature was clear at the temperature of 298° K. This confirms the assumption that the adsorption process with these soils does not include superficial adsorption on the surfaces of particles only the soil, but this is accompanied by slow processes of fixing potassium between the layers of clay minerals. In this regard, Strauss and Brummer (1989) indicated that the reaction of potassium with soil components includes an initial adsorption reaction, and this reaction is completed within minutes of its beginning and is then followed by a slower reaction. Increasing the temperature will increase the rate of reaction speed, which follows the surface adsorption process.

Table (5): Value of activity relative at equilibrium ($AR^0_K$) for three temperatures

| Depth | $AR^0_K \times (10^{-3})$ $mole.L^{-1/2}$ at temperature |
|---|---|

|  | 278° Kelvin | 298° Kelvin | 318° Kelvin |
|---|---|---|---|
| First Site |  |  |  |
| Surface | 2.02037 | 12.6901 | 10.2284 |
| Sub Surface | 1.61846 | 14.0517 | 10.0280 |
| Second Site |  |  |  |
| Surface | 6.2700 | 11.9736 | 8.3204 |
| Sub Surface | 2.3053 | 4.0018 | 3.6787 |
| Third Site |  |  |  |
| Surface | 3.0061 | 5.1187 | 8.3204 |
| Sub Surface | 4.0020 | 3.9602 | 3.6787 |

**4- Effect of temperature on free energy of potassium (ΔG)**

The free energy ΔG is one of the thermodynamic functions used to describe the spontaneity of the reaction because it represents the result of two factors: the change in heat capacity ΔH and the factor of change in the entropy of the reaction ΔS (Al-Obaidi et al., 2015), and the supply capacity of any soil can be found from the energy levels of the nutrients in the soil solution.

The level of this energy can represent the total differential of the supply forces of the element, which includes the nature of the ion, its salts, and its quality in relation to certain sites, as well as the ions accompanying it. It is possible to calculate the free energy from the following equation ($\Delta G = -RT \ln AR^0$) proposed by Woodruff (1955) based on evaluate the ionic activity ratios ($AR^0$) at equilibrium for potassium when no gain or loss occurs. A negative value for the amount of change in energy means that the reaction is spontaneous and does not require heat, while a positive value means that the reaction is non-spontaneous and requires heat. Through the results we obtained, it was shown that the values of the change in free energy ΔG for potassium in the study soil were all negative, which this means that the reaction is spontaneous.

Table (6) displays the results for free energy, from which it is noted that the values of change in the free energy of potassium $\Delta G_K$ in the soil ranged from ($-14.855\times10^{-3}$ kJ) in the subsurface depth of the first site to ($-11.724\times10^{-3}$ kJ) in the surface depth of the second site at a rate of ($-13.52\times10^{-3}$ kJ) at a temperature of 278° K, While the values ranged from ($-13.707\times10^{-3}$ kJ) in the subsurface depth of the third site to ($-10.568\times10^{-3}$ kJ) in the subsurface depth of the first site, and the average reached ($-12.133\times10^{-3}$ kJ), at a temperature of 298° K. As the temperature increased to 318° K, the values ranged from ($-14.821\times10^{-3}$ kJ) at the subsurface depth of the second site to ($-12.117\times10^{-3}$ kJ) at the surface depth of the first site, with an average of ($-13.19\times10^{-3}$ kJ).

Table (6): Value of free energy at equilibrium (ΔG) for three temperatures

| Depth | Free energy ($10^{-3}$) (Cal / $mole^{-1}$) at temperature |
|---|---|

| | 278° Kelvin | 298° Kelvin | 318° Kelvin |
|---|---|---|---|
| First Site | | | |
| Surface | -14.342 | -10.821 | -12.117 |
| Sub Surface | -14.855 | -10.568 | -12.170 |
| Second Site | | | |
| Surface | -11.724 | -10.965 | -12.663 |
| Sub Surface | -14.037 | -13.681 | -14.821 |
| Third Site | | | |
| Surface | -13.424 | -13.071 | -13.480 |
| Sub Surface | -12.762 | -13.707 | -13.898 |

This difference in the free energy values of the study soils is directly related to the equilibrium conditions between the soil solution and its solid phase, as well as to the difference in exchange sites and its mineral composition (Muhammadani, 2008). Negative values of free energy indicate a high available of the potassium ion, and the higher the value with a negative sign, the greater the availability of potassium quantitatively in the soil. Conversely, the greater the values of free energy with a positive sign mean a decrease in the available of potassium in those soils, which means the soil needs to add potassium ( Al-Obaidi et al., 2015).

**5- Effect of temperature on the entropy of potassium adsorption reactions ($\Delta S_K$):**

The entropy of the reaction ($\Delta S$) indicates the regularity and arrangement of the ions and is one of the thermodynamic functions, and the change in its value is a sensitive measure of any change in the structure of the system (Sparks, 2022). It was observed in table (7) that the increase in temperature led to making the interaction entropy values for all studied soils and for both depths less negative (higher reaction entropy values), which indicates the effect of temperature on the irregularity of potassium ions in the soil system and making them more entropy due to their higher internal energy due to the absorption of heat from the external environment affecting the reaction medium. The values of the entropy of the reaction at a temperature of 278° ranged from the highest value -53.43 expressed in joules.mol$^{-1}$ at the subsurface depth of the first site to the lowest value of -42.17 at the surface depth of the second site. While the increase in temperature to 298° led to an increase in the entropy values of the reaction system, the highest value of reaction entropy was recorded -45.99 in the subsurface depth of the third site and the lowest value of -35.46 in the subsurface depth of the first site. At 318° degrees, the highest value was -46.6 at the subsurface depth of the second site, and the lowest value was -38.10 at the surface depth of the first site. The change in the values of $\Delta S$ and its effect on the solubility of potassium-bearing minerals and its release from the solid soil phase and its transfer to the soil solution will cause a change in the arrangement of the reaction system. For example, when the value of the change in $\Delta S$ is negative, it indicates the spontaneity of the reaction (that is, the reaction It occurs naturally and does not require a catalyst and is a heat emitter) and the decrease in negativity of ΔS values will be with increasing temperature (Prasad and Sarangthem, 1992).

Table (7): Entropy values for adsorption reactions ($\Delta S_K$) for three temperatures

| Depth | Entropy of reaction (joule.mol$^{-1}$) at temperature | | |
|---|---|---|---|
| | 278° Kelvin | 298° Kelvin | 318° Kelvin |
| First Site | | | |
| Surface | -51.59 | -36.31 | -38.10 |
| Sub Surface | -53.43 | -35.46 | -38.27 |
| Second Site | | | |
| Surface | -42.17 | -36.79 | -39.82 |
| Sub Surface | -50.49 | -45.90 | -46.60 |
| Third Site | | | |
| Surface | -48.28 | -43.86 | -42.39 |
| Sub Surface | -45.90 | -45.99 | -43.70 |

## 6-Effect of temperature on enthalpy of potassium adsorption

Enthalpy refers to the heat released or absorbed during the process of dissolution or release and other reactions that occur in soil systems, and the change in enthalpy of the adsorption process is a measure of the heat of reaction. The results shown in table (8) show that all enthalpy values for the study samples were negative values, which indicates that the reaction is of the exothermic type, as when the temperature increases, the enthalpy values increase (the negativity of the values decreases). The highest negative value for enthalpy was observed at the temperature of 278° K was -29.70, expressed in kJ.mol$^{-1}$, at the subsurface depth of the first site, and the lowest negative value was -23.44, at the surface depth of the second site. When the temperature rose to 298° K, the highest value of enthalpy was -26.49 at the subsurface depth in the third location, and the lowest value was -20.42 in the subsurface depth in the first location, while the highest value of enthalpy at a temperature of 318° K reached -27.77 in the subsurface depth, for the second site, compared to the lowest value -22.70 at the surface depth for the first site. The high values of enthalpy of the potassium adsorption process from the liquid soil phase indicate that it may be due to the partial or complete removal of the aqueous shells of potassium, calcium, and magnesium ions (Appel et al., 2002).

Table (8): Enthalpy values for adsorption reactions ($\Delta H_K$) for three temperatures

| Depth | Enthalpy of reaction (K joule.mol$^{-1}$) at temperature | | |
|---|---|---|---|
| | 278° Kelvin | 298° Kelvin | 318° Kelvin |
| First Site | | | |
| Surface | -28.68 | -20.91 | -22.70 |
| Sub Surface | -29.70 | -20.42 | -22.80 |
| Second Site | | | |
| Surface | -23.44 | -21.19 | -23.73 |
| Sub Surface | -28.07 | -26.44 | -27.77 |
| Third Site | | | |
| Surface | -26.84 | -25.26 | -25.26 |
| Sub Surface | -25.52 | -26.49 | -26.04 |

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