

# Thermodynamic parameters of geochemical processes. The free energy of activation rather than the activation energy is the controlling factor\*

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**ABSTRACT:** In geochemical systems changes of phases may take place, ordering of ions, desorption, adsorption, formation or breaking of bonds, etc. that is, changes that result in change of the degrees of freedom of the systems. If the above changes happen during the “reactants” to “transition state or activated complex” step, then they result in changes in the entropy of activation. This information is included in the Free Energy of Activation,  $\Delta G^\ddagger$ . The Arrhenius and the Eyring equations relate the rate constant  $k$  of a process with the temperature  $T$ . In the Eyring equation the rate constant  $k$  is related to  $\Delta G^\ddagger$  that has a  $\Delta H^\ddagger$  and a  $\Delta S^\ddagger$  component. In the Arrhenius equation  $E_{act}$  is related to  $\Delta H^\ddagger$  and the pre-exponential factor  $A$  to  $\Delta S^\ddagger$ . If the activation energy value for a process is used, then there is relation of the rate constant only with the  $\Delta H^\ddagger$  component. If the free energy of activation value,  $\Delta G^\ddagger$ , is used, then there is relation of the rate constant to both components.

The application of the Eyring equation to literature data i.e. the calculation of  $\Delta H^\ddagger$  (that is related to  $E_{act}$ ),  $\Delta S^\ddagger$  (that is related to  $A$  of the Arrhenius equation) and  $\Delta G^\ddagger$  (combines  $E_{act}$  and entropy of activation) has pointed out that in geochemical transformations: there is a necessity to have the entropy value along with the enthalpy value of a process in the same factor ( $\Delta G^\ddagger$ ). Similar processes have similar  $\Delta G^\ddagger$  values. Thus, the Free Energy of activation rather than the Activation Energy is the controlling factor.

**Key-words:** activation energy, free energy of activation, enthalpy of activation, entropy of activation.

**ΠΕΡΙΛΗΨΗ:** Σε γεωχημικά συστήματα μπορούν να λάβουν χώραν μεταβολές φάσεων, διάταξη ιόντων, εκρόφιση, προσρόφιση, σχηματισμός ή διάσπαση δεσμών, κ.λπ. δηλαδή, μεταβολές που έχουν ως αποτέλεσμα την αλλαγή των βαθμών ελευθερίας των συστημάτων. Εάν οι παραπάνω μεταβολές συμβαίνουν κατά το στάδιο «αντιδρώντα» προς «μεταβατική κατάσταση ή ενεργοποιημένο σύμπλοκο», τότε οδηγούν σε μεταβολές στην εντροπία ενεργοποίησης. Αυτή η πληροφορία περιλαμβάνεται στην Ελεύθερη Ενέργεια Ενεργοποίησης, την  $\Delta G^\ddagger$ . Οι εξισώσεις Arrhenius και Eyring συσχετίζουν την σταθερά ταχύτητας  $k$  μίας διεργασίας με την θερμοκρασία  $T$ . Στην εξίσωση Eyring η σταθερά ταχύτητας  $k$  συσχετίζεται με την  $\Delta G^\ddagger$  η οποία έχει συνιστώσα  $\Delta H^\ddagger$  και  $\Delta S^\ddagger$ . Στην εξίσωση Arrhenius η  $E_{act}$  σχετίζεται με την  $\Delta H^\ddagger$  και ο προ-εκθετικός παράγων  $A$  με την  $\Delta S^\ddagger$ . Εάν επομένως χρησιμοποιείται η τιμή της ενέργειας ενεργοποίησης μιας διεργασίας τότε συσχετίζεται η σταθερά ταχύτητας μόνο με την  $\Delta H^\ddagger$  συνιστώσα. Εάν χρησιμοποιείται η τιμή της ελεύθερης ενέργειας ενεργοποίησης τότε υπάρχει συσχέτιση της σταθεράς ταχύτητας και με τις δύο συνιστώσες.

Η εφαρμογή της εξίσωσης Eyring σε δεδομένα της βιβλιογραφίας δηλαδή ο υπολογισμός της  $\Delta H^\ddagger$  (η οποία σχετίζεται με την  $E_{act}$ ), της  $\Delta S^\ddagger$  (η οποία σχετίζεται με τον  $A$  της εξίσωσης Arrhenius) και  $\Delta G^\ddagger$  (η οποία συνδέει την  $E_{act}$  μέσω της  $\Delta H^\ddagger$  και την εντροπία ενεργοποίησης) έχει δείξει ότι σε γεωχημικές μετατροπές: είναι αναγκαίο να υπάρχει η τιμή της εντροπίας μαζί με την τιμή της ενθαλπίας μιας διεργασίας στον ίδιο παράγοντα ( $\Delta G^\ddagger$ ). Παρόμοιες διεργασίες έχουν παρόμοιες τιμές  $\Delta G^\ddagger$ . Έτσι, η ελεύθερη ενέργεια ενεργοποίησης μάλλον παρά η ενέργεια ενεργοποίησης είναι ο ρυθμιστικός παράγων.

**Λέξεις-κλειδιά:** ενέργεια ενεργοποίησης, ελεύθερη ενέργεια ενεργοποίησης, ενθαλπία ενεργοποίησης, εντροπία ενεργοποίησης.

## INTRODUCTION

Many authors describe and discuss the various geochemical transformations presenting and commenting on the activation energy values that are calculated for the processes. Examples of the literature where the Activation Energies were discussed along with other significant factors that played important roles in the processes are presented in this work. All the other factors i.e. adsorption, formation or breaking of bonds, change of phases, ordering of ions etc., which are related to the change of degrees of freedom of the transformations, are factors that are included in the Entropy of Activation  $\Delta S^\ddagger$  of a process. The Entropy of Activation along

with the Enthalpy of Activation  $\Delta H^\ddagger$ , which is related to the Activation Energy by the relation  $\Delta H^\ddagger = E_{act} - RT$  constitute the components of the Free Energy of Activation  $\Delta G^\ddagger$  according to the thermodynamic relation  $\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$ . Our aim in this paper is to calculate the Enthalpies of Activation, the Entropies of Activation and the Free Energies of Activation of certain processes that have been described in the literature, and prove that the Free Energy of Activation rather than the Activation Energy is the controlling factor for geochemical processes/transformations to take place. The Free Energy of Activation describes fully the systems since it combines both the Activation Energy (through the  $\Delta H^\ddagger$  component) and the change in the degrees of freedom that result from the

\* Θερμοδυναμικές παράμετροι γεωχημικών διεργασιών. Η ελεύθερη ενέργεια ενεργοποίησης μάλλον παρά η ενέργεια ενεργοποίησης είναι ο ρυθμιστικός παράγων

transformations (through the  $\Delta S^\ddagger$  component). The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  can be obtained by applying the Eyring equation to the data. Then the  $\Delta G^\ddagger$  at certain temperature can be calculated.

Some excellent examples of the literature where the authors comment on the significance of the “entropic contribution” either through calculating the A factor of the Arrhenius equation or through calculating the entropy of activation factor of the Lassaga equation, are treated and discussed in this work through the Eyring equation in which both the enthalpy of activation and the entropy of activation are included in the free energy of activation term.

The activation energy for the  $\alpha$ -NiS oxidation in the temperature range 670-700 °C is reported (WANG *et al.*, 2006) to be  $E_{act} = 868.2 \text{ kJmol}^{-1}$ . Applying the Arrhenius and the Eyring equation to the data of the above publication we found (see below, example I)  $E_{act} = 839.7 \text{ kJmol}^{-1}$ ,  $\Delta G^\ddagger = 326.5 \text{ kJmol}^{-1}$  at 948 K. The effect of the entropic component is obvious:  $\Delta S^\ddagger = 532.6 \text{ J K}^{-1} \text{ mol}^{-1}$ .

The dissolution of natural barite cleavage fragments over the temperature range 44-85 °C showed an activation energy value of  $24.9 \pm 10.1 \text{ kJmol}^{-1}$ . Barite growth from supersaturated aqueous solutions (precipitation) showed  $E_{act} = 22.0 \pm 14.3 \text{ kJmol}^{-1}$  (CHRISTY & PUTNIS, 1993). Our calculations (see below, example II) give values of  $\Delta G^\ddagger$  for dissolution =  $94.8 \text{ kJmol}^{-1}$  at 333 K. The  $\Delta S^\ddagger$  for dissolution is  $-218.6 \text{ J K}^{-1} \text{ mol}^{-1}$  and plays a significant role. The  $\Delta G^\ddagger$  of precipitation is  $63.8 \text{ kJmol}^{-1}$  at 333 K with  $\Delta S^\ddagger = -170.4 \text{ J K}^{-1} \text{ mol}^{-1}$ .

For the transformation of synthetic mackinawite to hexagonal pyrrhotite (LENNIE *et al.*, 1995) it is stated that “the value obtained for  $E_{act}$  in the present study is high in comparison with the activation energies of most solid-state processes (PUTNIS, 1992)...” The activation energy that was obtained for the above experiment was  $493 \text{ kJmol}^{-1}$  with a frequency factor (A of the Arrhenius equation) of  $3.7 \times 10^{45} \text{ min}^{-1}$ . Of course the authors comment on the significance of the A value that is related (see below “The Arrhenius versus the Eyring equation”) to the entropy of activation. Our calculations (see below example III) using the data of the above work give  $\Delta G^\ddagger = 175.5 \text{ kJmol}^{-1}$  at 540 K. The strong entropic contribution is also calculated.

In the presentation of the exsolution of pentlandite  $(\text{Ni,Fe})_9\text{S}_8$  from the monosulfide solid solution  $(\text{Fe,Ni})\text{S}$  (ETSCHMANN *et al.*, 2004) it is stated that “...the activation energy for exsolution of pentlandite from mss  $\text{Fe}_{0.8}\text{Ni}_{0.2}\text{S}$  between 473 and 423 K is  $5 \text{ kJ mol}^{-1}$ . Most solid-state processes in silicate and oxysalt minerals have activation energies between about 200 and 400  $\text{kJ mol}^{-1}$  with a moderate reaction velocity  $k = 10^{-10}$  to  $10^{-15} \text{ s}^{-1}$  (PUTNIS, 1992). In this sulfide system the exsolution of pentlandite from mss is very rapid with high reaction velocities of  $10^{-5}$  to  $10^{-6} \text{ s}^{-1}$  and an activation energy of less than  $10 \text{ kJ mol}^{-1}$ . Such figures point to relatively high mobility of metal ions at ambient temperatures, a finding consistent with that of FARRELL & FLEET (2002) who noted exsolution of Co-pentlandite from mss in samples stored at room temperatures for 34 months.” Our calculations

(see below, example IV) give  $\Delta G^\ddagger = 234.6 \text{ kJmol}^{-1}$  at 640 K for mss composition  $\text{Fe}_{0.9}\text{Ni}_{0.1}\text{S}$  and  $226.4 \text{ kJmol}^{-1}$  at 640 K for mss composition  $\text{Fe}_{0.8}\text{Ni}_{0.2}\text{S}$ . At temperature 298 K our calculations (see below, example IV) give  $\Delta G^\ddagger = 90.7 \text{ kJmol}^{-1}$  for  $\text{Fe}_{0.9}\text{Ni}_{0.1}\text{S}$  and  $99.7 \text{ kJmol}^{-1}$  for  $\text{Fe}_{0.8}\text{Ni}_{0.2}\text{S}$ . The calculated negative values of the enthalpies of activation and the significant contributions of the entropies of activation are discussed.

We could present a lot of other important examples from the literature i.e. the nucleation of hematite (pH 10.7), pure goethite (pH 13.7) and phosphate-doped goethite (pH 13.7) and their crystallization (SHAW *et al.*, 2005), the study of schwertmannite transformation to goethite and hematite under alkaline conditions (DAVIDSON *et al.*, 2008), the ferrihydrite transformation to goethite via the Fe(II) pathway (YEE *et al.*, 2006), the cation ordering in synthetic  $\text{MgAl}_2\text{O}_4$  spinel (ANDREOZZI & PRINCIVALLE, 2002), the cation ordering in natural  $\text{Mg}(\text{Al,Cr}^{3+})_2\text{O}_4$  spinels (PRINCIVALLE *et al.*, 2006) etc. where the activation energy of a geochemical process is presented and discussed but we will focus only on the above examples in order to prove the necessity of the use of  $\Delta G^\ddagger$  instead of the Activation energy  $E_{act}$ . That is, we will show that the Free Energy of Activation rather than the Activation Energy is the controlling factor in geochemical transformations since in these transformations the contribution of the entropic factor could be significant and this factor is included in  $\Delta G^\ddagger$ .

## THE ARRHENIUS VERSUS THE EYRING EQUATION

Both the Arrhenius 
$$k_{obs} = A e^{-\frac{E_{act}}{RT}} \quad (1)$$

and the Eyring 
$$k = \kappa \frac{RT}{Nh} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (3)$$

equations describe the temperature dependence of the reaction rate constant (ESPENSON, 1981; KATAKIS, 1987; PETROU & ECONOMOU-ELIOPOULOS, 2009). The Arrhenius equation strictly speaking can be applied to the kinetics of reactions in the gas phase. The Eyring equation can be used in the study of solution reactions and in mixed phase reactions that is in all processes where the simple collision theory is not helpful.

The Free energy of activation  $\Delta G^\ddagger$  includes not only the  $\Delta H^\ddagger$  component ( $= E_{act} - RT$ ) but also the  $\Delta S^\ddagger$  component that may be important. The term  $-T\Delta S^\ddagger$  that has to be added to  $\Delta H^\ddagger$  in order to give  $\Delta G^\ddagger$  may be critical i.e. in various examples below. Thus the entropic contribution may be severe and may give answers to many questions arising in an attempt to explain geological phenomena.

TABLE 1

Data for the  $\alpha$ -NiS oxidation in the temperature range 670–700 °C (WANG *et al.*, 2006).

$k$ ( $s^{-1}$ )	$T$ (K)	$1/T$ ( $K^{-1}$ )	$\ln(k/T)$	$\ln k$
$1.2 \times 10^{-5}$	943	0.00106	-18.18	-11.33
$3.3 \times 10^{-5}$	953	0.00105	-17.18	-10.32

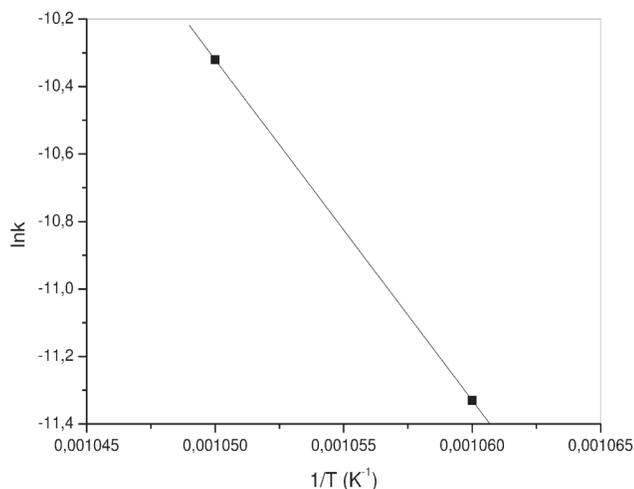


Fig. 1. Arrhenius plot of the data of Table 1.

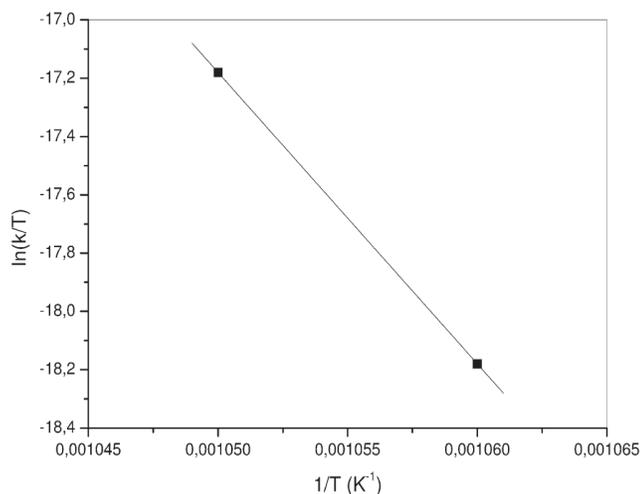


Fig. 2. Eyring plot of the data of Table 1.

## IMPORTANT EXAMPLES

### I. The $\alpha$ -NiS oxidation in the temperature range 670–700 °C

Experimental data support that the reaction mechanism in the temperature range 670 to 680 °C is constant with  $E_{act}=868.2$   $\text{kJmol}^{-1}$  (WANG *et al.*, 2006). The transformation of the temperature (°C) to absolute (K) are given in Table 1.

“The reaction mechanism in the temperature range 670–680 °C is constant with  $E_{act}=868.2$   $\text{kJ mol}^{-1}$ ”. The change in

TABLE 2

Data for the Barite dissolution in water and sodium chloride brines at 44–85 °C (CHRISTY & PUTNIS, 1993).

$\theta$ (°C)	$k$ ( $\text{L m}^2 \text{s}^{-1}$ )
$45.1 \pm 0.5$	$0.0095 \pm 0.0003$
$45.3 \pm 0.4$	$0.0036 \pm 0.0008$
$55.1 \pm 0.4$	$0.0058 \pm 0.0008$
$64.6 \pm 0.2$	$0.0132 \pm 0.0004$
$74.1 \pm 1.1$	$0.0128 \pm 0.0005$
$70.4 \pm 1.4$	$0.0192 \pm 0.0009$
$44.8 \pm 0.2$	$0.0084 \pm 0.0014$
$70.6 \pm 1.8$	$0.0100 \pm 0.0004$
$67.5 \pm 1.1$	$0.0099 \pm 0.0016$

the entropy of activation going from reactants to the transition state is very positive, meaning that in the transition state there is less organization than in the reactants. The values of  $k$ 's that are given in the publication are  $3.3 \times 10^{-5} \text{s}^{-1}$  at 680 °C and  $1.2 \times 10^{-5} \text{s}^{-1}$  at 670 °C. Application of both the Arrhenius and the Eyring equations to these data is presented in Figs 1 & 2.

From the Arrhenius plot (Fig. 1) we calculate  $E_{act}$  and  $A$ :  
 $E_{act} = 839.7$   $\text{kJ mol}^{-1}$ ,  $A = 3.76 \leftrightarrow 10^{41} \text{s}^{-1}$

From the Eyring plot (Fig. 2) we calculate  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ .  $\Delta G^\ddagger$  is then calculated at 675 °C = 948 K

$\Delta H^\ddagger = 831.4$   $\text{kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 532.6$   $\text{J K}^{-1} \text{mol}^{-1}$ ,  $\Delta G^\ddagger = 326.5$   $\text{kJ mol}^{-1}$  at 675 °C = 948 K

It can be noticed that the entropy of activation value is very large.

### II. Barite dissolution and precipitation in water and sodium chloride brines at 44–85 °C

The dissolution of natural barite cleavage fragments over the temperature range 44–85 °C showed activation energy of  $24.9 \pm 10.1$   $\text{kJmol}^{-1}$  (CHRISTY & PUTNIS, 1993). Barite growth from supersaturated aqueous solutions (precipitation) showed  $E_a = 22.0 \pm 14.3$   $\text{kJmol}^{-1}$  (CHRISTY & PUTNIS, 1993).

#### I. Dissolution experiments (Table 2)

The authors state: “An Arrhenius plot for the rate constants of Table 2 was conducted. Although there is considerable scatter ( $r = 0.68$ ), a general trend of increasing rate with increasing temperature is discernible, and linear regression gives an activation energy of  $24.9 \pm 10.1$   $\text{kJmol}^{-1}$  ... This value

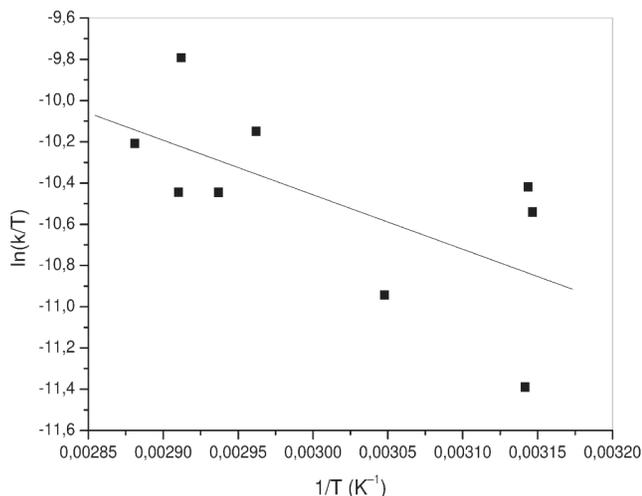


Fig. 3. Eyring plot of the data of Table 2.

for the activation energy could correspond to either bulk diffusion (16–20 kJmol<sup>-1</sup>) or desorption (>35 kJmol<sup>-1</sup>: BERNER, 1978; NIELSEN, 1984; ZHANG & NANCOLLAS, 1990) as the rate-controlling step, both of which are consistent with the first-order rate law”...“...bulk diffusion is too fast to be a rate-limiting process”... “Barite dissolution in our experiments is likely to be desorption controlled”.

Transforming the temperature (°C) to absolute temperature (K) and ignoring standard deviations we apply the Eyring equation to the above data (Fig 3).

$$\Delta H^\ddagger = 22.0 \pm 10.1 \text{ kJmol}^{-1}, \Delta S^\ddagger = -218.6 \pm 30.3 \text{ JK}^{-1}\text{mol}^{-1},$$

$$\Delta G^\ddagger = 94.8 \text{ kJmol}^{-1} \text{ at } 333 \text{ K}$$

$$\Delta G^\square = 87.1 \text{ kJmol}^{-1} \text{ at } 298 \text{ K}$$

The strong contribution of the  $\Delta S^\ddagger$  could be noticed. This contributes in the value of  $\Delta G^\ddagger$ . The  $\Delta S^\ddagger$  of dissolution is negative,  $-218.6 \pm 30.3 \text{ JK}^{-1}\text{mol}^{-1}$ , meaning that going from the “reactants” to the transition state there is a degree of organization. The final state that is the “products” of dissolution, it

TABLE 3

Data for the Barite precipitation in water and sodium chloride brines at 44–85 °C (CHRISTY & PUTNIS, 1993).

$\theta$ (°C)	$k$ (L <sup>2</sup> s <sup>-1</sup> m <sup>-2</sup> mol <sup>-1</sup> )
43.7 ± 0.2	1757 ± 226
44.0 ± 0.3	193 ± 13
46.8 ± 0.3	477 ± 16
66.2 ± 1.3	343 ± 23
68.7 ± 1.0	2302 ± 74
76.0 ± 0.3	786 ± 72
85.0 ± 0.9	663 ± 55

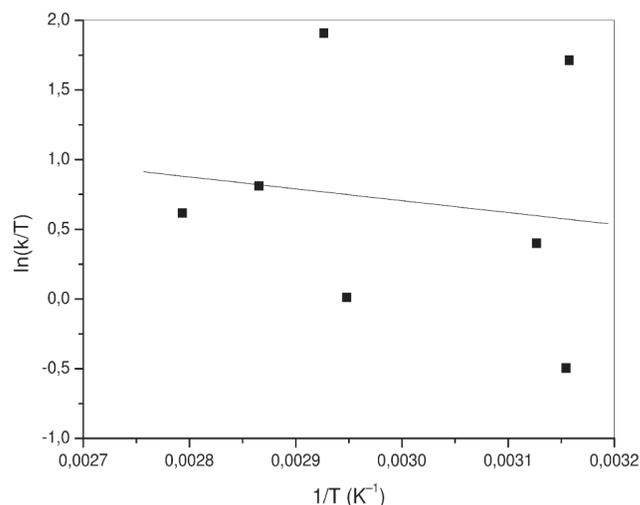


Fig. 4. Eyring plot of the data of Table 3.

is obvious that bears  $\Delta S^0 > 0$ , meaning less organization, more degrees of freedom than the starting “reactants”. The negative value found above corresponds to the process reactants to transition state and suggests a great degree of organization before the final “products”.

## II. Precipitation experiments (Table 3)

Transforming the temperature (°C) to absolute temperature (K) and ignoring standard deviations we apply the Eyring equation to the above data (Fig. 4).

$$\Delta H^\ddagger = 7.1 \pm 21.3 \text{ kJmol}^{-1}, \Delta S^\ddagger = -170.4 \pm 64.0 \text{ JK}^{-1}\text{mol}^{-1},$$

$$\Delta G^\ddagger = 63.8 \text{ kJmol}^{-1} \text{ at } 333 \text{ K (60 °C)}$$

The contribution of the  $\Delta S^\square$  could again be seen contributing in the value of  $\Delta G^\square$ .

The authors of the paper discard the rate-constants that were calculated at  $\Theta = 43,7$  °C and  $\Theta = 68,7$  °C as “anomalously large”. They state: “If the two anomalously large rate constants from two experiments (runs 27 and 33) are discounted, then the activation energy for precipitation is calculated as  $22.0 \pm 14.3 \text{ kJmol}^{-1}$  by linear fit ( $r = 0.75$ ) to an Arrhenius plot, and the extrapolated rate constant at 25 °C is  $162 \pm 65 \text{ l}^2\text{s}^{-1}\text{m}^{-2}\text{mol}^{-1}$ ...” “The second-order rate law for precipitation is compatible with either surface diffusion or integration at the growth site being the rate-limiting process (NIELSEN, 1984; ZHANG & NANCOLLAS, 1990). The uncertainty in activation energy is too large to distinguish these alternatives”.

In Fig. 5, we also discard these two values, as the authors did.

$$\Delta H^\ddagger = 19.2 \pm 11.2 \text{ kJmol}^{-1}, \Delta S^\ddagger = -138.2 \pm 33.3 \text{ JK}^{-1}\text{mol}^{-1},$$

$$\Delta G^\ddagger = 65.2 \text{ kJmol}^{-1} \text{ at } 333 \text{ K}$$

$$\text{and } \Delta G^\square = 60.4 \text{ at } 298 \text{ K}$$

The contribution of the  $\Delta S^\ddagger$  to the value of  $\Delta G^\ddagger$  could again be noticed.  $\Delta S^\ddagger$  of precipitation is negative suggesting that going from the “reactants” to the transition state there is

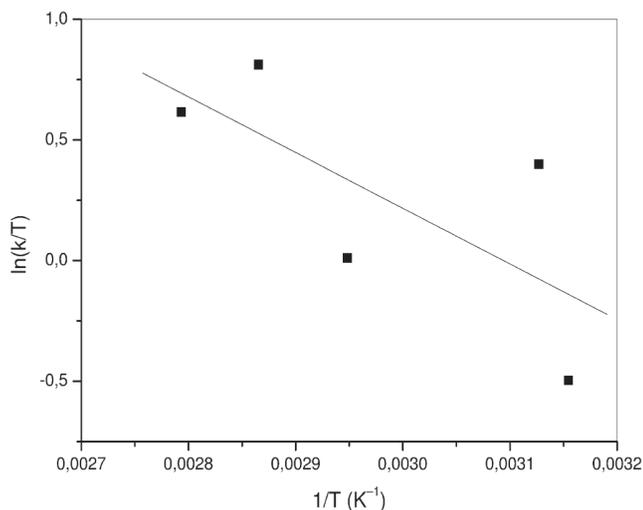


Fig. 5. Eyring plot of the data of Table 3 after discarding the data at  $\Theta=43,7^\circ\text{C}$  and  $\Theta=68,7^\circ\text{C}$ .

a degree of organization. According to the authors: “Activation energies for the two processes are fortuitously similar ( $24,9\pm 10,1\text{ kJmol}^{-1}$  for dissolution,  $22,0\pm 14,3\text{ kJmol}^{-1}$  for precipitation)... Comparison with the results of LIU & NANCOLLAS (1975) suggests that ... rough barite surfaces. There is some evidence that precipitation from highly supersaturated solutions ... involves polynuclear growth on grain surfaces and homogeneous nucleation of new particles, both of which would cause ...”. The polynuclear growth (if it takes place on going from the “reactants” to the transition state) is a reason for decreasing the entropy of activation since the polymerization decreases the degrees of freedom.

### III. Transformation of synthetic mackinawite to hexagonal pyrrhotite

Experiments conducted by researchers (LENNIE *et al.*, 1995) in the temperature range 530-545 K give rate constants from which an activation energy of  $493\text{ kJ mol}^{-1}$  and a frequency factor of  $3.7\leftrightarrow 10^{45}\text{ min}^{-1}$  (Arrhenius equation) have been established. The mechanism proposed for this transformation is that of a solid-state diffusion process.

Treatment of the experimental data that are presented in the above publication according to the Eyring equation (our suggestion) leads to:  $\Delta H^\ddagger = 422.6\text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = 457.6\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $\Delta G^\ddagger$  (at 540K) =  $175.5\text{ kJ mol}^{-1}$ . ( $T\Delta S^\ddagger = 540\text{ K} \leftrightarrow 457.6\text{ J K}^{-1}\text{ mol}^{-1} = 247104\text{ J mol}^{-1} = 247.1\text{ kJ mol}^{-1}$  and  $\Delta H^\ddagger - T\Delta S^\ddagger = 422.6\text{ kJ mol}^{-1} - 247.1\text{ kJ mol}^{-1} = 175.5\text{ kJ mol}^{-1}$ ).  $\Delta G^\ddagger$  (at 530K) =  $180.1\text{ kJ mol}^{-1}$ .  $\Delta G^\ddagger$  (at 500K) =  $193.8\text{ kJ mol}^{-1}$  (Table 4, Fig. 6).

$$\Delta H^\ddagger = 422.6 \pm 5.6\text{ kJmol}^{-1}, \Delta S^\ddagger = 491.6 \pm 10.4\text{ J K}^{-1}\text{ mol}^{-1}$$

Correction for the value of  $\Delta S^\ddagger$  is needed since the rate constant in the publication is given in  $\text{min}^{-1}$  and in transforming it to  $\text{s}^{-1}$  units we must divide by 60. Thus from the value  $\Delta S^\ddagger = 491.6\text{ J K}^{-1}\text{ mol}^{-1}$  the  $\ln 60 \leftrightarrow 8.31 = 34$  must be subtracted to give  $\Delta S^\ddagger = 457.6\text{ kJ mol}^{-1}$ . Thus  $\Delta G^\ddagger$  (at 540K) =

TABLE 4  
Data for the transformation of synthetic mackinawite to hexagonal pyrrhotite (LENNIE *et al.*, 1995).

$\ln k$	$T$ (K)	$1/T$ ( $\text{K}^{-1}$ )	$\ln(k/T)$
-3.82	545	0.00183	-10.12
-5.39	537	0.00186	-11.68
-6.90	530	0.00189	-13.17

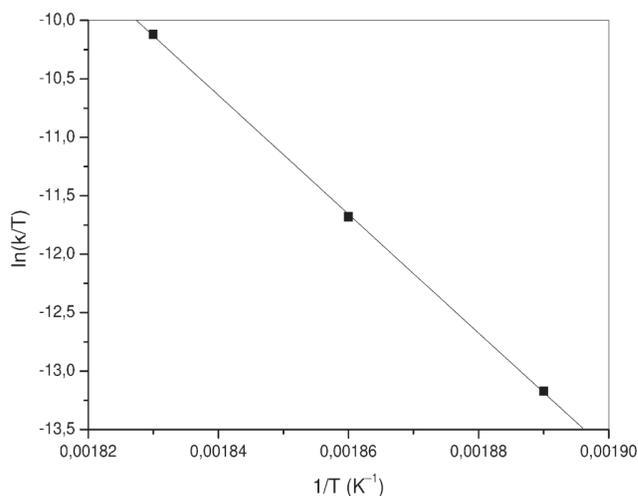


Fig. 6. Eyring plot of the data of Table 4.

$175.5\text{ kJ mol}^{-1}$ .

In conclusion the Free Energy of Activation for the above transformation is:

$$\Delta G^\ddagger \text{ (at 540K)} = 175.5\text{ kJ mol}^{-1} \quad \Delta G^\ddagger \text{ (at 530K)} = 180.1\text{ kJ mol}^{-1} \quad \Delta G^\ddagger \text{ (at 500K)} = 193.8\text{ kJ mol}^{-1}$$

The authors state that “the value obtained for  $E_{\text{act}}$  in the present study ( $493\text{ kJ mol}^{-1}$ ) is high in comparison with the activation energies of most solid-state processes (PUTNIS, 1992)...”

If we consider the Free Energy of activation value instead of the Activation Energy, that is,  $175.5\text{ kJ mol}^{-1}$  (at 540K) instead of  $493\text{ kJmol}^{-1}$  we can realize that the entropic contribution is substantial ( $T\Delta S^\ddagger = 540\text{ K} \leftrightarrow 457.6\text{ J K}^{-1}\text{ mol}^{-1} = 247.1\text{ kJ mol}^{-1}$ ). Breaking of bonds during the Reactants to transition state process leads to positive  $\Delta S^\ddagger$ , hence negative  $-T\Delta S^\ddagger$  which is subtracted from  $\Delta H^\ddagger$  (that is related to  $E_{\text{act}}$ ) and so the Free Energy  $\Delta G^\ddagger$  becomes smaller than the Activation Energy.

The positive  $\Delta S^\ddagger > 0$  suggests a Dissociative mechanism (PETROU & ECONOMOU-ELIOPOULOS, 2009).

### IV. Exsolution of pentlandite $(\text{Ni,Fe})_9\text{S}_8$ from the monosulfide solid solution $(\text{Fe,Ni})\text{S}$

“...the activation energy for exsolution of pentlandite from mss  $\text{Fe}_{0.8}\text{Ni}_{0.2}\text{S}$  between 473 and 423 K is  $5\text{ kJ mol}^{-1}$ . Most solid-state processes in silicate and oxysalt minerals have ac-

TABLE 5

Data for the exsolution of pentlandite (Ni,Fe)<sub>9</sub>S<sub>8</sub> from the monosulfide solid solution (Fe,Ni)S. Mss (monosulfide solid solution) composition Fe<sub>0.9</sub>Ni<sub>0.1</sub>S (ETSCHMANN *et al.*, 2004).

$k$ (s <sup>-1</sup> )	$T$ (K)	$1/T$ (K <sup>-1</sup> )	$\ln(k/T)$
$6 \times 10^{-6}$	473	0.00211	-18.18285
$2 \times 10^{-6}$	773	0.00129	-19.77264
$6 \times 10^{-8}$	823	0.00122	-23.34188

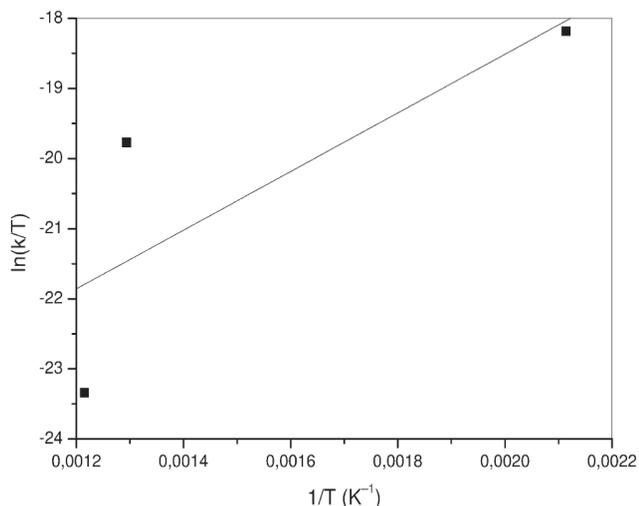


Fig. 7. Eyring plot of the data of Table 5.

tivation energies between about 200 and 400 kJ mol<sup>-1</sup> with a moderate reaction velocity  $k=10^{-10}$  to  $10^{-15}$  s<sup>-1</sup> (PUTNIS, 1992). In this sulfide system the exsolution of pentlandite from mss is very rapid with high reaction velocities of  $10^{-5}$  to  $10^{-6}$  s<sup>-1</sup> and activation energy of less than 10 kJ mol<sup>-1</sup>. Such figures point to relatively high mobility of metal ions at ambient temperatures, a finding consistent with that of FARRELL & FLEET (2002) who noted exsolution of Co-pentlandite from mss in samples stored at room temperature for 34 months” (ETSCHMANN *et al.*, 2004). The exsolution of pentlandite from mss/pyrrhotite involves two main processes, nucleation and growth, each with its own activation energy.

Our calculations using the data of ETSCHMANN *et al.* (2004), revealed:

### I. Mss (monosulfide solid solution) composition

#### Fe<sub>0.9</sub>Ni<sub>0.1</sub>S (Table 5, Fig. 7)

$\Delta H^\ddagger = -34.8 \pm 27.1$  kJ mol<sup>-1</sup>,  $\Delta S^\ddagger = -421.0 \pm 43.2$  J K<sup>-1</sup> mol<sup>-1</sup>,  
 $\Delta G^\ddagger = 234.6$  kJ mol<sup>-1</sup> at  $T=640$  K  $\Delta G^\ddagger = 90.7$  kJ mol<sup>-1</sup> at  $T=298$  K

### II. Mss (monosulfide solid solution) composition

#### Fe<sub>0.8</sub>Ni<sub>0.2</sub>S (Table 6, Fig. 8)

$\Delta H^\ddagger = -10.6 \pm 4.4$  kJ mol<sup>-1</sup>,  $\Delta S^\ddagger = -370.3 \pm 7.9$  J K<sup>-1</sup> mol<sup>-1</sup>,

TABLE 6

Data for the exsolution of pentlandite (Ni,Fe)<sub>9</sub>S<sub>8</sub> from the monosulfide solid solution (Fe,Ni)S. Mss (monosulfide solid solution) composition Fe<sub>0.8</sub>Ni<sub>0.2</sub>S (ETSCHMANN *et al.*, 2004)

$k$ (s <sup>-1</sup> )	$T$ (K)	$1/T$ (K <sup>-1</sup> )	$\ln(k/T)$
$7 \times 10^{-6}$	423	0.00236	-17.91697
$8 \times 10^{-6}$	473	0.00211	-17.89516
$2 \times 10^{-6}$	853	0.00117	-19.87112
$6 \times 10^{-6}$	873	0.00115	-18.79569

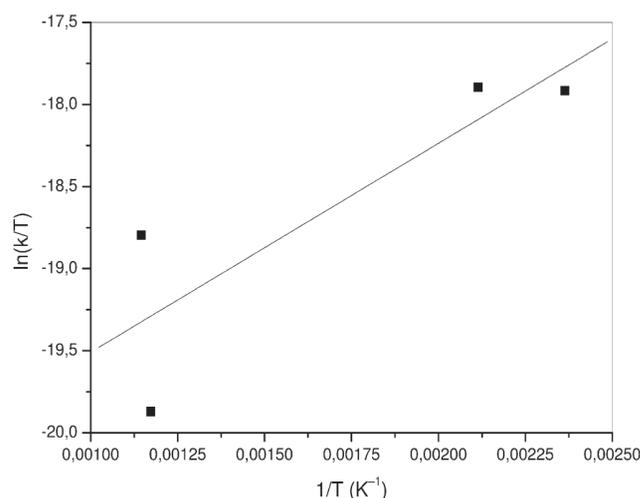


Fig. 8. Eyring plot of the data of Table 6.

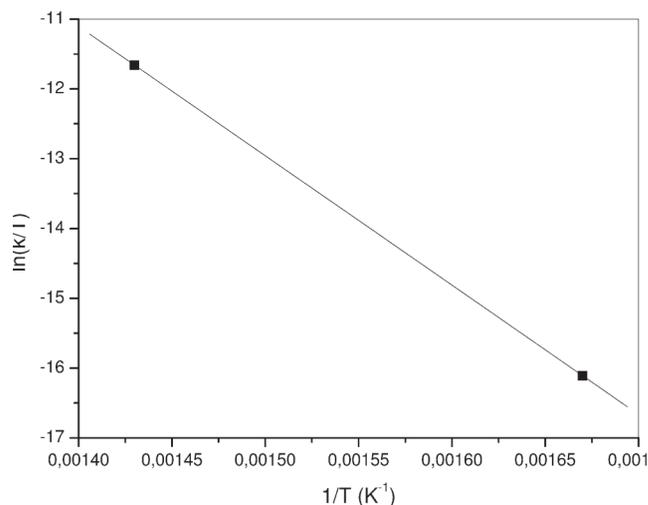


Fig. 9. Eyring plot of the data for the exsolution of pyrite from pyrrhotite.

$\Delta G^\ddagger = 226.4$  kJ mol<sup>-1</sup>  $T=640$  K

$\Delta G^\ddagger = 99.7$  kJ mol<sup>-1</sup> at  $T=298$  K

The authors report that: “YUND & HALL (1970) investigated the exsolution of pyrite from pyrrhotite. Using their

data, rate constants can be calculated for the exsolution of pyrite from pyrrhotite of bulk composition  $\text{Fe}_{0.862}\text{S}$ . At 698K,  $k = 6 \times 10^{-3} \text{ s}^{-1}$  and at 598K,  $k = 6 \times 10^{-5} \text{ s}^{-1}$  with  $n=0.2$  for both temperatures. The approximate activation energy, calculated by using an Arrhenius plot for these two rate constants, is  $163 \text{ kJ mol}^{-1}$ . We applied the Eyring equation to these data. In Fig. 9, the plot of  $\ln k/T = f(1/T)$  gives  $\Delta H^\ddagger = 154.2 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -74.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta G^\ddagger = 202.2 \text{ kJ mol}^{-1}$  at  $T = 648 \text{ K}$

$\Delta H^\ddagger = 154.2 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -74.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta G^\ddagger = 202.2 \text{ kJ mol}^{-1}$  at 648 K,  $\Delta G^\ddagger = 176.3 \text{ kJ mol}^{-1}$  at  $T = 298 \text{ K}$

## Summarising:

### I. Mss (monosulfide solid solution) composition

$\text{Fe}_{0.9}\text{Ni}_{0.1}\text{S}$

$\Delta H^\ddagger = -34.8 \pm 27.1 \text{ kJ mol}^{-1}$

$\Delta S^\ddagger = -421.0 \pm 43.2 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta G^\ddagger = 234.6 \text{ kJ mol}^{-1}$  at  $T = 640 \text{ K}$   $\Delta G^\ddagger = 90.7 \text{ kJ mol}^{-1}$  at  $T = 298 \text{ K}$

### II. Mss (monosulfide solid solution) composition

$\text{Fe}_{0.8}\text{Ni}_{0.2}\text{S}$

$\Delta H^\ddagger = -10.6 \pm 4.4 \text{ kJ mol}^{-1}$

$\Delta S^\ddagger = -370.3 \pm 7.9 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta G^\ddagger = 226.4 \text{ kJ mol}^{-1}$  at  $T = 640 \text{ K}$   $\Delta G^\ddagger = 99.7 \text{ kJ mol}^{-1}$  at  $T = 298 \text{ K}$

### III. Exsolution of pyrite from pyrrhotite.

$\Delta H^\ddagger = 154.2 \text{ kJ mol}^{-1}$

$\Delta S^\ddagger = -74.0 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta G^\ddagger = 202.2 \text{ kJ mol}^{-1}$  at 648 K  $\Delta G^\ddagger = 176.3 \text{ kJ mol}^{-1}$  at  $T = 298 \text{ K}$

Completely different are the values especially for  $\Delta H^\ddagger$  (large positive value) compared to negative values for cases I and II. The entropy of activation value is negative but a lot smaller than in cases I and II. The  $\Delta G^\ddagger$  value at 640 K compares well with the values found for cases I and II.

The negative values of  $\Delta H^\ddagger$  are explained as follows: (an) exothermic process(es), that is, processes with negative enthalpies of reactions, precede the rate-determining process and the enthalpy of activation for the total transformation is equal to the algebraic sum of the various enthalpies that accompany all the processes that are involved. If one exothermic process precedes the rate-determining one, then the  $\Delta H^\ddagger$  is given by the sum:  $\Delta H^\ddagger = \Delta H^0 + \Delta H^\ddagger_{\text{r.d.s.}}$  where  $\Delta H^0$  is negative (the enthalpy of the exothermic process) and  $\Delta H^\ddagger_{\text{r.d.s.}}$  is the activation enthalpy for the rate-determining step which is positive. When the absolute value of  $\Delta H^0$  is greater than the value of  $\Delta H^\ddagger_{\text{r.d.s.}}$  then the result of the total  $\Delta H^\ddagger$  is negative. The consequence of this result is the decrease of the rate of the reaction with increasing temperature.

## CONCLUSION

The application of the Eyring equation to literature data i.e. the calculation of  $\Delta H^\ddagger$  (that is related to  $E_{\text{act}}$ ),  $\Delta S^\ddagger$  (that is re-

lated to A of the Arrhenius equation) and  $\Delta G^\ddagger$  (combines  $E_{\text{act}}$  and entropy of activation) has pointed out that in geochemical transformations:

There is a necessity to have the entropy value along with the enthalpy value of a process in the same factor ( $\Delta G^\ddagger$ ).

- There is explanation why certain activation energy values (that are related to enthalpy of activation values) for certain transformations deviate from expected energy values when the entropic component is substantial.

- The Free Energy of activation rather than the Activation Energy is the controlling factor.

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