

# An investigation on solvent extraction of oil from Egyptian oil-shale

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In the present work a study of the extraction of oil from oil shale supplied by Red-See Phosphate-company, using methylene chloride (boiling rang 40-45 °C) was performed. The aim of this initial research was to determine the effects of the main factors, which can potentially influence the extraction of oil. The factors involved in this study were particle size, temperature, solvent-feed ratio (S/F) and the mixing intensity. Oil extraction rate was found to be diffusion-controlled (the activation energy was found to be 3.73 kJ/gm). Mass Transfer coefficient of the process under different conditions and the thermodynamic parameters were also determined.

في هذه الدراسة تم دراسة استخلاص المادة الزيتية من القشور الزيتية المصرية المستخرجة بواسطة شركة فوسفات البحر الأحمر باستخدام مذيب كلوريد الايثيلين (درجة الغليان تتراوح ما بين 40-45 °C). الهدف من هذه الدراسة هو تحديد تأثير المؤثرات التي يمكنها أن تؤثر علي عملية الاستخلاص. من المؤثرات التي تم دارستها هي حجم الحبيبات ، درجة الحرارة ، نسبة المادة الصلبة إلى المذيب (S/F) و معدل التقليب . وقد تم معادلة هذه العوامل . وقد وجد أن معدل الاستخلاص محكوم بالانتشارية (حيث أن طاقة التنشيط تساوي 3.73 كيلو جول/جرام). وتم أيضا إيجاد معامل الانتقال للكتلة و قيم بعض الدوال الترموديناميكية.

**Keywords:** Oil Shale, Solvent extraction, Kinetics study, Thermodynamic parameters, Activation energy

## 1. Introduction

The oil crisis of the early 1970s saw many multinational oil companies and government agencies investing large sums of money into oil shale research and development as an alternative hydrocarbon sources. Red-See Phosphate-company, Egypt supplies the oil-shale from Ras-Showkar. The shale contains an organic material that called kerogen. This is a heterogeneous mixture of organic mineral that can be dissolved by organic solvent and extracted from oil shale [1]. Three major steps can judge the extraction of the oil from the oil shale. First, the kerogen is dissolved by the solvent on the surface of the particle transferring its solid phase into liquid phase. Second, forward diffusion of the solvent through the pores of the particles is taken place and also another dissolution takes place inside the particles. Third, a backward diffusion and mass transfer of the solution from the core of the particles to the main bulk of the solution is followed [2-6]. Any one of these three steps can be limiting steps. The

first step is usually fast if the proper solvent was used. The second step is also fast if the particles have large pores and solvent viscosity and surface tension are low. Third, there is backward diffusion and mass transfer of this solution to main bulk of solution flow. The third step will be fast if turbulence and agitation are high enough to increase the mass transfer convection processes [7-9].

Porosity and pore size distribution greatly affect the rate of oil extraction because the solvent must flow or diffuse in and out of the pores, and sometimes the solute moves through the pores to the particle surface by diffusion [10].

Shale oil comes from oil shale, but oil shale is a misnomer. It is neither a true shale nor does it generally have any oil in it. It is better identified geologically as organic marlstone because of their large percentage of carbonates.

Duncan and Swanson [11] stated that, the US Geological survey defines the oil shale as "organic-rich shale that yield substantial quantities of oil by conventional methods of

destructive distillation of the contained organic matter, which employ low confining pressures in a closed retort system". They further define oil shale for purposes of their report to "any part of an organic-rich shale deposit that yields at least 10 gallons (3.8 percent) of oil per short ton of shale.

Anabtawi [12] reported that the oil shale is composed of about 86% mineral matter and 14% organic matter, however, the organic matter should not exceed 25%. The organic matter in the oil shale is composed of bitumen, about 10-20% and rarely exceeding 20% and kerogen, about 80-90%. Bitumen is a heteroatomic polymer, which is soluble in many organic solvents but has a high percentage of sulfur content and therefore can be extracted for hydrocarbon recovery and sulfur retention. Kerogen is a heteroatomic polymer and is insoluble in most organic solvents, therefore it cannot be extracted for oil utilization.

The volume of literature from the world on shale oil recovery is huge. Clearly there has been no lack of talented effort. Colorado School of mines scientists and engineers, with the huge oil shale deposits virtually in their back yard, have been most diligent in pursuing all aspects of this problem [13-14].

Tamimi and Uysal [15] investigated different parameters that affected the extraction of El-lajjun oil shale with organic solvent in continuous stirred tank reactor (CSTR) using a mixture of solvent (75% benzene and 25% cyclohexane).

Skala et al. [16] studied the rate of pyrolysis and oxidation of 8 different samples of oil shale kerogen concentrate (KC) using DSC and TG analysis. They indicated that the activation energy of the pyrolysis of specific KCs increases with increasing paraffinic structure in the KC.

Dung [17] studied seven process variables-retort, temperature, solid recycle ratio, char content recycle solids, temperature, pretreatment of recycle solids with ammonia, solids residence time and steam concentration using Plackett-Burman statistical experimental design.

Oil shale in Egypt was taken from upper cretaceous outcrops and cores of this age.

The only economic use of the oil shale seems to be their direct combustion in the

electric power plant or their use in the cement production.

The Aim of this work is to investigate the extraction of oil from oil shale and to study the different parameters affecting extraction, determination of thermodynamic parameters and mass transfer coefficients.

## 2. Materials and experiments

### 2.1. Materials

The oil shale of Red Sea Phosphate Company- Ras-Showkar provided the following ultimate analysis:

| Carbon | Hydrogen | Nitrogen | Sulfur | Moisture | Ashes |
|--------|----------|----------|--------|----------|-------|
| 17.3   | 1.82     | 0.69     | 0.66   | 0.4      | 67.3  |

The oil shale samples were prepared by grinding and sieving using Rotap Sieve Shaker. Fraction between average size 0.26 mm and 1.6 mm were collected. Different solvents methylene chloride, dimethyl formamid and petroleum ether were tested since the extracted material, bitumen, remained in the solution at the room temperature and pressure. Using soxhlet apparatus, it was found that the methylene chloride (boiling range 40-45 °C) gave highest extraction yield (about 10.64 % by weight of solid oil shale) through this work. Analytical grade methylene chloride was used and purified after each run by distillation in Rotary vacuum distillation column.

### 2.2. Equilibria of oil extraction

Quick fit bottles (250 ml), each containing 2 gm of crushed oil shale. An appropriate amount of solvent of methylene chloride (boiling range 40-45 °C) was added to each of the bottles that were then sealed. The samples were brought to the extraction temperature and shaken at 150 rpm. in a thermostated water-bath for at least 210 min. Extract were obtained, and the oil content in the extract was measured spectrophotometrically [17], (MSE Spectro-plus MKIA supplied by MSE Scientific Instruments, England) using 0.5 light path glass cell at  $\lambda_{\max} = 380 \text{ nm}$ .

Extraction samples were replicated three times for each of the experimental conditions. The final results are given as mean values of replicated samples. The same procedure was used to obtain equilibrium data at other regulated temperatures of extraction.

### 2.3. Rate of oil extraction

A 2 gm of oil shale was extracted in a sealed bottle shaken by a thermostated shaking water-bath. The temperature of the extractor was maintained in a water-bath at the required extraction temperature. Extraction was terminated after a desired period of time and the oil content was determined.

### 2.4. Oil content of oil-shale

Using soxhlet apparatus, the total oil-content in oil shale was determined by exhausting selective amount of oil shale with different batches of pure solvent (keeping temperature at 35 °C and time for 3 hr for each batch [11]) and the amount of extract determined in each batch was calculated. Under these conditions, it was found that the methylene chloride gave about 10.64 % by weight that represents about 72% from the original amount of oil.

## 3. Results and conclusions

### 3.1. Particle size effect on the extraction rate

The particle size is a significant parameter in the extraction of oil shale. It is a direct function of the total surface area per unit volume of solids. Effect of Particle Size (PS) on oil-extraction rate from oil shale was shown in fig. 1, at which increasing the particle size decrease the rate of oil extraction from the bulk of oil shale, fig. 1 shows that the maximum rate of extraction was obtained at the particle size equal to 0.25 mm.

The experimental studies carried by Tamimi and Uysal [14] indicate that the range of particle size suitable for extraction was between 0.2 to 2 mm in diameter. If the particle size is less than 0.2 mm, the problems

of agglomeration and coagulation impede agitation, hinder dissolution and obstruct the percolation process. For particles larger than 2 mm, the extraction rate is essentially constant and slows [14].

Rate constant for the effect of particle size was obtained from results in figs. 2 and 3. The slopes of straight lines fig. 2 represent the rate constants  $k$  of the extraction rate. Fig. 3 shows that the relationship between the rate constant and the particle sizes can be expressed by the following equation:

$$K_{PS} = -1.659(PS)^{-0.2003} \quad (1)$$

### 3.2. Temperature effect on the extraction rate

Increasing the temperature decrease the adhesiveness, viscosity, and surface tension of the oil contained in the shale but increase its diffusivity and its mobility from the shale.

The effect of temperature on the extraction rate of oil from oil shale is shown in fig. 4, it is seen that with increasing the temperature the rate of oil extraction from the bulk seeds increases. Also, it shows that the increase in the rate of extraction of oil at higher temperature reduces the time necessary to attain equilibrium. However, the maximum rate of extraction was obtained at the temperature of 40 °C, care should be taken that the boiling range of methylene chloride is 40-45 °C

Fig. 4 shows that at certain temperature (e.g. 40 °C), the rate of extraction increased sharply with increasing the time, and then remains constant after 60 min. The rate may be expressed in terms of square root of time [18] as depicted in fig. 5.

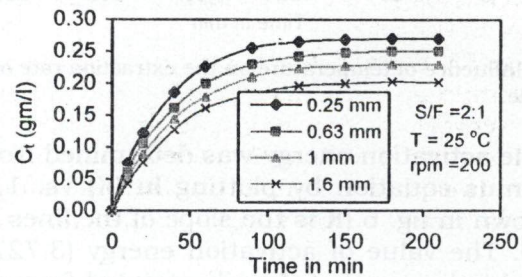


Fig. 1. Particle size effect on the extraction rate of oil from shale oil.

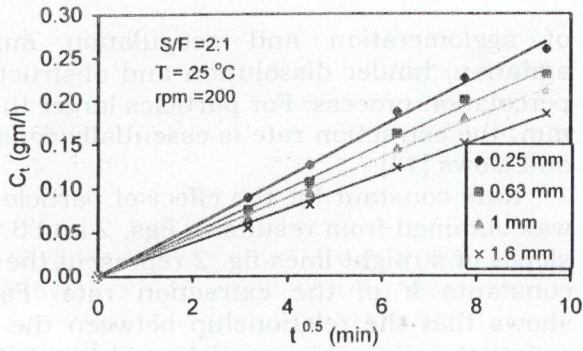


Fig. 2.  $C_t$  vs. the square root of the contact time ( $t^{0.5}$ ) for various particle sizes.

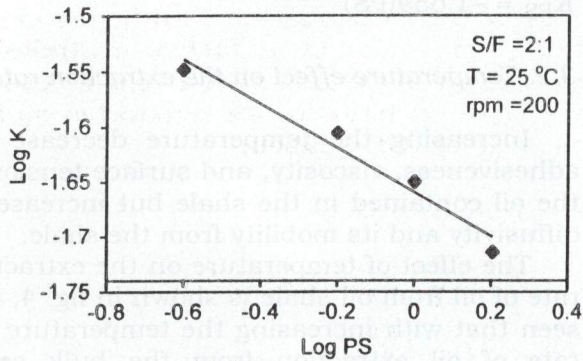


Fig. 3. Logarithmic rate parameter against logarithmic particle sizes (PS).

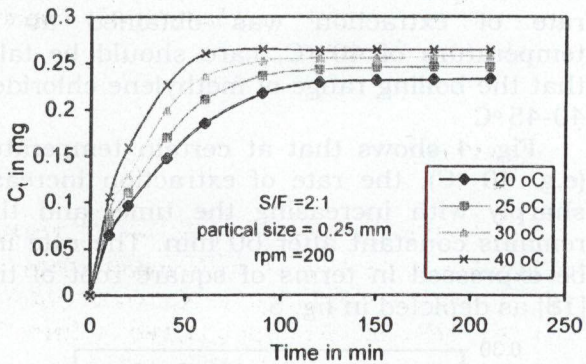


Fig. 4. Influence of temperature on the extraction rate of oil shale.

The activation energy was determined from Arrhenius equation by plotting  $\ln(K)$  vs.  $1/T$  as shown in fig. 6 ( $K$  is the slope of the lines in fig. 5). The value of activation energy (3.7274 kJ/gm) indicates that the oil extracted from oil shale using methylene is a diffusion-controlled process [19, 20]. The choride effect of the

temperature on extraction-rate parameter can be expressed by the following equation;

$$K_{PS} = 9.781(T(^{\circ}K))^{-1.876} \quad (2)$$

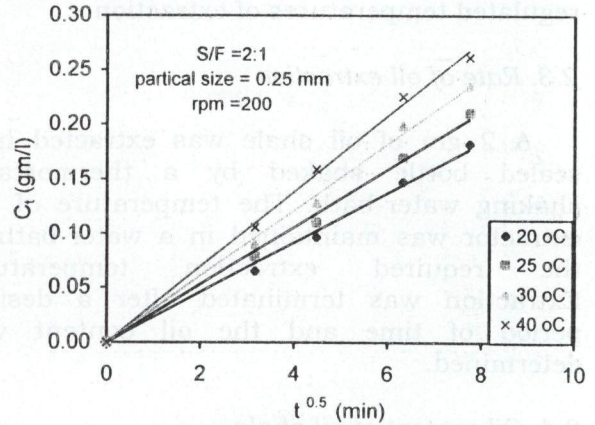


Fig. 5. Extracted oil ( $C_t$ ) against the square root of the contact time ( $t^{0.5}$ ) for various temperatures.

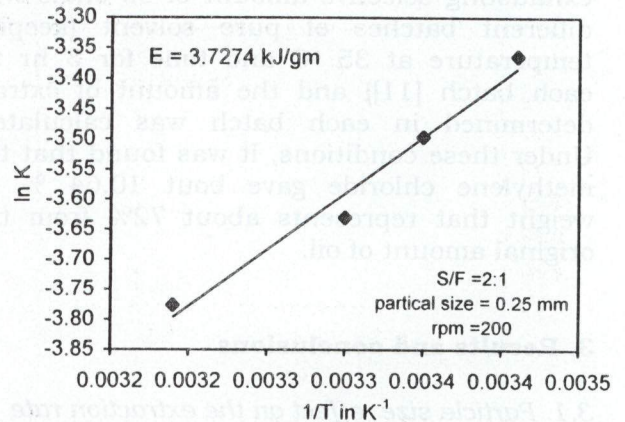


Fig. 6. Activation energy curve for oil shale extraction.

### 3.3. Solvent-feed ratio (S/F) effect on the extraction rate

The weight of solvent used per kilogram of oil shale is denoted by S/F ratio. The quantity of solvent should be enough to impregnate all the oil-shale particles with solvent. The behavior of extraction rate with different solvent-feed (S/F) weight ratio is shown in fig. 7. The concentration of oil extracted from the oil shale in solvent decrease with increasing the S/F ratio, but on the other

hand the amount of oil extracted is increased. The increment in the concentration of the oil after time = 80 min was very small. This proves that the optimum time for extraction is 80 min.

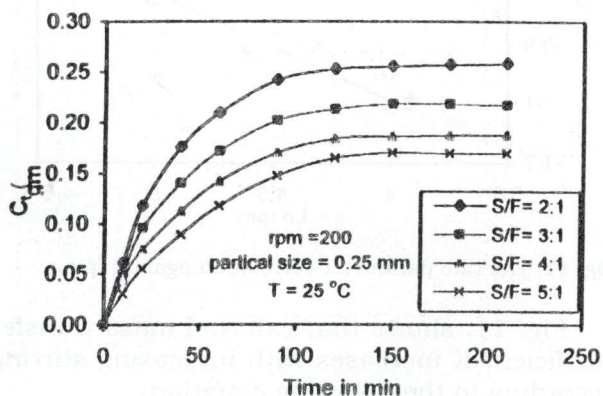


Fig. 7. Effect of solvent-feed ratios (S/F) on the extraction rate.

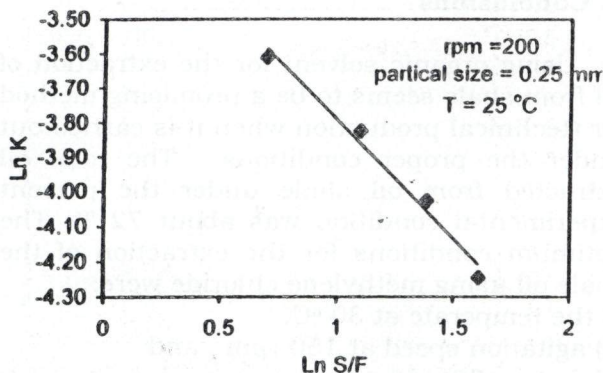


Fig. 8. Rate parameter relationship with solvent-feed ratio (S/F).

The solvent-feed ratio dependence of K was determined by plotting log (S/F) as shown in fig. 8. The data fit the equation,

$$K_{(S/F)} = 3.1124 (S/F)^{-0.818} \quad (3)$$

### 3.4. Mixing intensity effect (rpm.) on the extraction rate

Mixing increase the extraction rate due to increasing the degree of turbulence [5] as shown in fig. 9. Thus the rate of extraction is determined by one or more of the following:

- 1-Mass transfer of solvent from the bulk solution to the particle surface,
- 2-Intraparticle diffusion, and
- 3-Dissolution of oil from the inner pores.

Step 3 is assumed to be rapid [24] and should not be considered in any kinetic analysis. Consequently, the two rate limiting steps considered are external mass transport and intraparticle diffusion. At the beginning of the diffusion process, it can be assumed that the solvent moves first of all from the solution toward the surface of oil shale and thus all mass transfer is restricted to the external boundary layer [24].

For the batch reactor used in the present work, the rate of diffusion controlled of extraction of oil from oil shale can be expressed in terms of the removal of oil from oil shale by the equation;

$$-V(dC/dt) = kAC \quad (4)$$

which upon integration yields,

$$\ln(C_0/C) = kAt/V \quad (5)$$

where A is the total outer surface of the particles, can be determined from the mass m and particles density  $\rho_t$ , of solid used by assuming spherical particles of constant diameter dp; that is:

$$A = \frac{6m}{\rho_t dp(1-t)} \quad (6)$$

Fig. 10 showed a typical  $\ln(C_0/C)$  versus t relation for extraction of oil from oil shale. The mass transfer coefficients K, was obtained from the slop of the  $\ln(C_0/C)$  vs. t line. The curve is characterized by two distinct rates; the development of models based on two such mass transport steps is quite complex requiring a simplifying assumption as shown by Furusawa and Smith [24]. They assumed that external mass transport of fresh solvent from the bulk of solution across the boundary layer film to the external particle surface is rate controlling in the early stage of the extraction process. In the present work, the increase in the rate of mass transfer (external mass transfer) in the first stage of extraction

of oil from oil shale as result of stirring was considered for quantitative treatment.

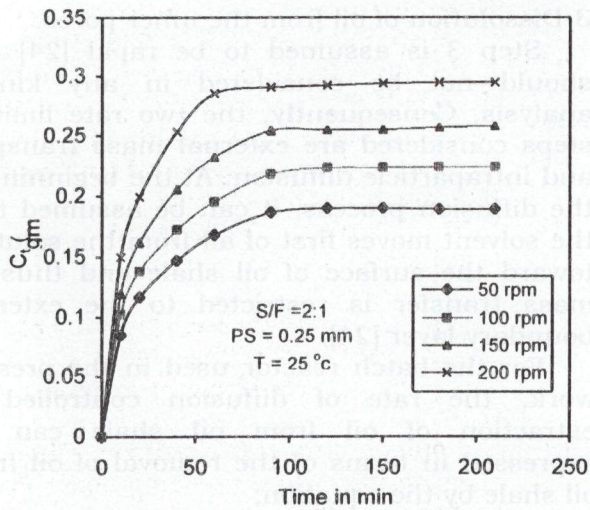


Fig. 9. Effect of mixing intensity on the extraction rate of oil.

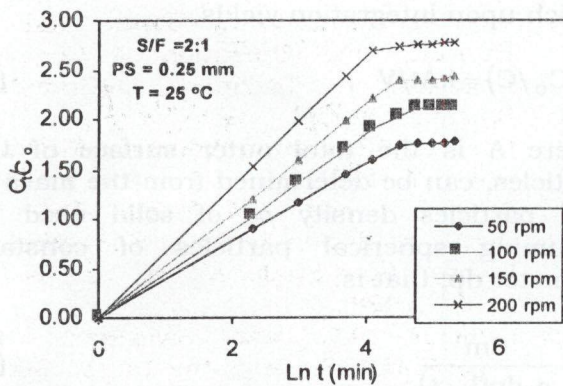


Fig. 10.  $(C_t/C_0)$  against the logarithmic time  $(\ln t)$  for various rpm.

3.5. Thermodynamic parameters calculation

Thermodynamic data can be derived from the above results using the equations shown in the appendix. The values of the Gibbs free energy, activation energy, enthalpy and entropy [21, 22] are reported in table 2.

Table 2  
Thermodynamic parameters of oil extraction from shale

| Temp. °K | K min <sup>-1</sup> | $E$ kJ/gmol | $\Delta H$ kJ/gmol | $\Delta S$ kJ/gmol. °K | $\Delta G^0$ kJ/gmol |
|----------|---------------------|-------------|--------------------|------------------------|----------------------|
| 293.15   | 0.0346              | 1.9584      | 1.372              | -12.8615               | 8.881                |
| 298.15   | 0.0303              | 2.0704      | 1.478              | -12.560                | 9.121                |
| 303.15   | 0.0265              | 2.1858      | 1.584              | -11.750                | 9.365                |
| 313.15   | 0.0229              | 2.3488      | 1.727              | -11.259                | 9.785                |

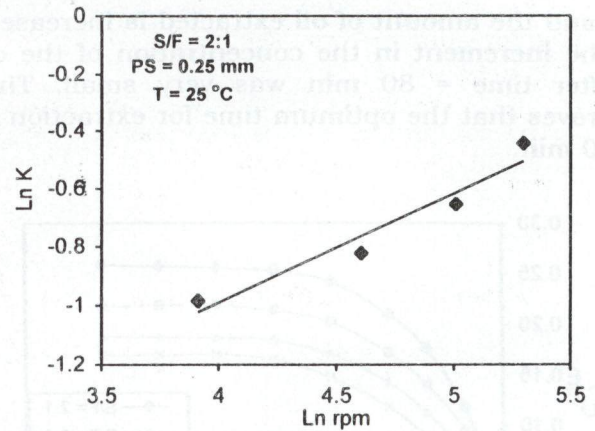


Fig. 11. The rate parameter correlation against rpm..

Fig. 11. shows that external mass transfer coefficient  $K$  increases with increasing stirring according to the following equation;

$$K_{(rpm)} = -2.4786(rpm)^{0.3723} \quad (7)$$

5. Conclusions

Using organic solvent for the extraction of oil from shale seems to be a promising method for technical production when it is carried out under the proper conditions. The total oil extracted from oil shale under the present experimental condition was about 72 %. The optimum conditions for the extraction of the shale oil using methylene chloride were:

- (i) the temperate at 30 °C,
- (ii) agitation speed at 150 rpm., and
- (iii) time = 80 min.

The major part of the oil was found to be extracted from the surface of the shale rather than from its pores (activation energy was 3.73 kJ/gmol). The rate extraction was

expressed as functions of particle size, temperature, solvent-feed ratio and mixing intensity.

The thermodynamic functions such as activation energy, Gibbs free energy, enthalpy and entropy were determined.

## Appendix

### 1. Evaluation of activation energy (E)

$$K = A \exp(-E/RT)$$

where:

A = Boltzman constant

R = Universal gas constant (1.987 cal . deg<sup>-1</sup> . mol<sup>-1</sup>)

### 2. Evaluation of the free energy

$$K = \frac{AT}{h} \cdot e^{-(\Delta G^0 / RT)}$$

where h is Plank's quantum constant

### 3. Evaluation of enthalpy

$$\Delta H = -R \frac{d \ln(K/T)}{d(1/T)}$$

$$E = H + RT$$

### 4. Evaluation of entropy

$$K = \frac{AT}{h} e^{\Delta S / R} e^{-\Delta H / RT}$$

## Nomenclature

|                 |  |
|-----------------|--|
| A               | surface area of mass transfer, cm <sup>2</sup> , |
| C               | concentration at any time t, mg/l,               |
| C <sub>0</sub>  | initial dichromate concentration, mg/l,          |
| K               | mass transfer coefficient, cm/sec,               |
| E               | activation Energy, kJ/gmol,                      |
| ΔG <sup>0</sup> | gibbs free energy, kJ/gmol.K,                    |
| ΔH              | enthalpy, kJ/gmol,                               |
| ΔS              | entropy, kJ/gmol,                                |
| t               | the time, min,                                   |
| T               | temperature, K,                                  |
| V               | volume of liquid, cm <sup>3</sup> , and          |
| ρ               | density of solution, gm/cm <sup>3</sup> .        |

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