

APPLICATION OF GRAPHICAL AND ANALYTICAL METHODS IN THE DETERMINATION OF THE ACTIVATION ENERGY USING THE ARRHENIUS EQUATION

Yousuo Digieneni¹, Orlando Ketebu² and Omuso-Wilson Ereyanannyo³

^{1,3}Department of Petroleum Engineering, Niger Delta University, P.M.B 071 Yenagoa, Bayelsa State of Nigeria.

²Department of Chemical Engineering, Niger Delta University, P.M.B 071 Yenagoa, Bayelsa State of Nigeria

¹ E-mail: digienenyousuo@yahoo.com;

ABSTRACT

A simple definition of the activation energy is given. Factors affecting the activation energy of a reaction are mentioned. It is also stated that Activation energy does not depend upon the temperature, pressure, volume, concentration, or coefficients of reactant. The Arrhenius equation that shows the dependence of chemical rates on temperature is given. The activation energy from the Arrhenius equation was determined by both the graphical method and analytical method. For reactants A and B both having a concentration of 1.0 mol/dm³ which is exothermic and proceeds 100 times faster at 400K than 300K, the activation energy determined through the graphical method is 47844.825J/mol and that which is determined through the analytic method is 45931.032J/mol.

Keywords: *Activation Energy, Arrhenius Equation, Temperature, Reaction Rate, Gas Constant.*

INTRODUCTION

Activation energy is the minimum amount of energy required for a chemical reaction to take place. Activation energy depends on two factors: The Nature of Reactants and Effect of Catalyst. Activation energy does not depend upon the temperature, pressure, volume, concentration, or coefficients of reactant.

The quantitative dependence of chemical rates on temperature most commonly noticed is given by the empirical Arrhenius equation

$$K \propto n_0 e^{-k/RT} \quad \text{or} \quad K = Ae^{-E/RT}$$

(1)

Where

- K = specific rate constant
- A = proportionality constant
- n_o = number of moles
- R = Gas constant = 8.31J/K
- T = Temperature in Kelvin (K)
- E = activation Energy

Generally, a 10°C rise in reaction temperature increases the reaction rate by a factor of 2 or 3. This increase cannot be said to have been caused by the increased kinetic energy of the gas due to the temperature rise, as the kinetic energy increases only by about 3% for the same temperature rise (Audu, 1991; Himmelblau, 1974; Levenspiel, 1962; Cooper and Jeffreys, 1973).

MATERIALS AND METHODS

When equation (1) is expressed logarithmically, the Arrhenius equation becomes

$$\ln K = A - E / RT \quad (2)$$

$$2.303 \log_{10} K = A - E / RT \quad (3)$$

$$\Rightarrow \log_{10} K = \frac{A}{2.303} - \frac{E}{2.303RT} \quad (4)$$

A plot of $\log_{10} K$ against $1/T$ should be a straight line whose slope is $-E/2.303R$ as shown in figure 1.0

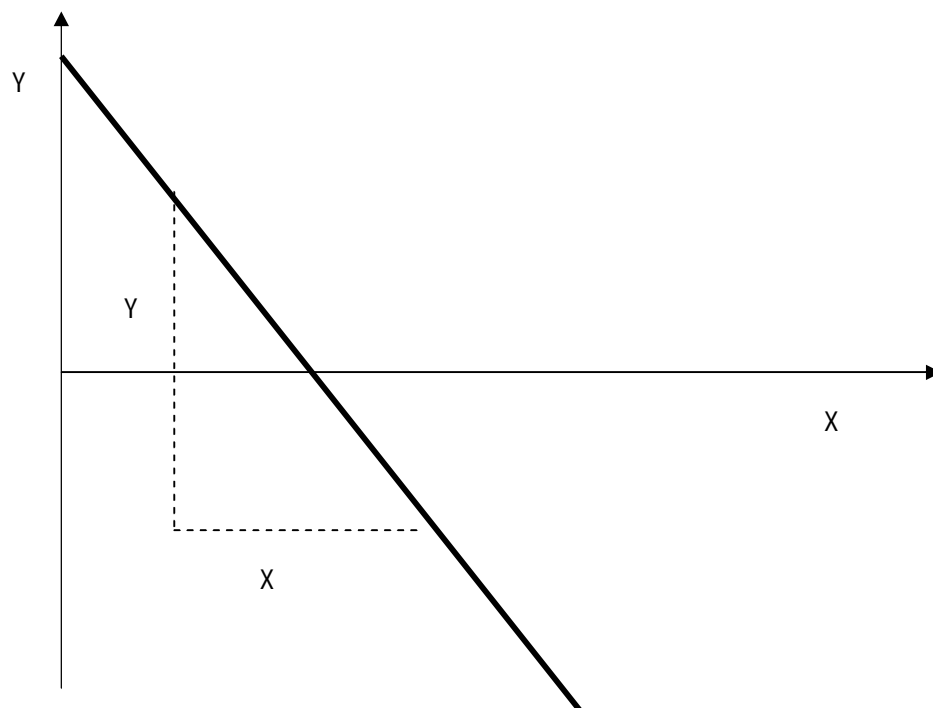
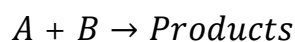


Figure 1.0: The graph of $\log_{10} K$ against $1/T$

Figure 1.0 shows that the slope is Y/X or $-E/2.303R$

Let us now consider the hypothetical gaseous reaction:



(5)

If we are to determine graphically using the Arrhenius equation, the activation energy of the reaction assuming that A and B both have a concentration of 1.0 mol/dm^3 and equation (5) is exothermic and proceeds 100 times faster at 400K than 300K.

The graphical method

So we use the graphical method to determine the activation energy as follows:

Using equation (3) and (4)

$$2.303 \log_{10} K = A - E / RT$$

$$\Rightarrow \log_{10} K = \frac{A}{2.303} - \frac{E}{2.303RT}$$

$$\text{Rate of reaction} = k[A][B] \quad (6)$$

$$k = \frac{\text{Rate of reaction}}{[A][B]} \quad (7)$$

From what is given:

$$[A] = [B] = 1.0 \text{ mol/dm}^3 \quad (8)$$

$$\Rightarrow k = \text{Rate of reaction} \quad (9)$$

Since the rate of reaction proceeds 100 times faster at 400K than at 300K, we can form the table of value as shown in Table 1.0

If at 300K the rate of reaction is 10s^{-1} then at 400K the rate of reaction is 100 times 10 which is equal to 1000s^{-1}

Using equation (4),

$$\log_{10} k = \frac{\text{Constant}}{2.303} - \frac{E}{2.303RT}$$

Table 1.0: Table of temperature (K) and rate of reaction (k) Values

Temperature, T (K)	1/T	Rate of reaction, k(s^{-1})	$\log_{10} k$
300	0.0033	10	1
400	0.0025	1000	3

If we plot $\log_{10} k$ against $1/T$, the slope of the graph = $\frac{-E}{2.303R}$ and the intercept of the graph is equal to $\frac{\text{Constant}}{2.303}$

The plot is shown in figure 2.0

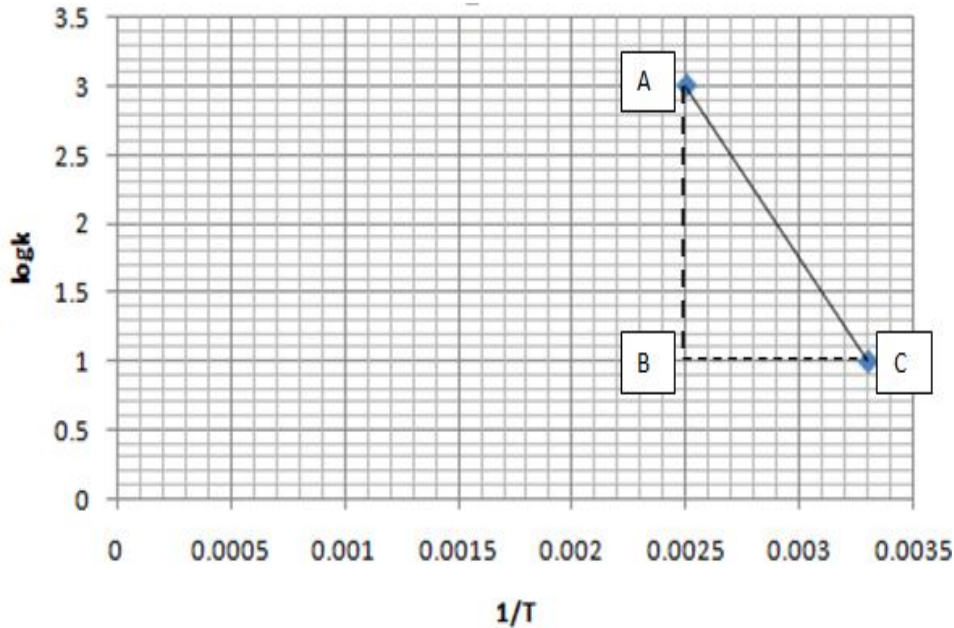


Figure 2.0: The plot of \log_{10}^k against $1/T$

Considering figure 2.0,

The *Slope* of the graph

$$\begin{aligned}
 &= \frac{AB}{BC} \\
 &= \frac{3.0-1.0}{0.0025-0.0033} \\
 &= \frac{2}{-0.0008} \\
 &= -2500 \\
 &= -2500
 \end{aligned}$$

$$\Rightarrow \frac{-E_a}{2.303R}$$

Therefore, E
 Since $R = 8.31\text{J/K}$

E

E

$$= (2.303 \times R)(2500)$$

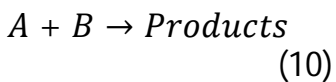
$$= (2.303 \times 8.31)(2500)$$

$$= 47844.825\text{J/mol}$$

Therefore, the activation energy determined from the graphical method is 47844.825J/mol

Analytical Method

We can as well use analytical methods to determine the activation Energy as follows:



$$2.303 \log_{10} k = \text{constant} - \frac{E_a}{RT} \quad (11)$$

$$\log_{10} k = \frac{\text{Constant}}{2.303} - \frac{E_a}{2.303RT} \quad (12)$$

$$\log_{10} k_1 = \frac{\text{Constant}}{2.303} - \frac{E_a}{2.303RT_1} \quad (13)$$

$$\log_{10} k_2 = \frac{\text{Constant}}{2.303} - \frac{E_a}{2.303RT_2} \quad (14)$$

Substituting equation (13) in (14) gives

$$\log_{10} k_2 - \log_{10} k_1 = \frac{E_a}{2.303RT_1} - \frac{E_a}{2.303RT_2} \quad (15)$$

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303RT_1} - \frac{E_a}{2.303RT_2} \quad (16)$$

$$\text{But } r = kC_A C_B \quad (17)$$

So $r = k$ since $C_A = C_B = 1.0 \text{ mol/dm}^3$

$$\text{And } r_1 = k_1 \quad \text{at } 300\text{K} \quad (18)$$

$$r_2 = k_2 \quad \text{at } 400\text{K} \quad (19)$$

$$\text{But } k_2 = 100k_1 \quad (20)$$

$$\Rightarrow \log_{10} \frac{100k_1}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{300} - \frac{1}{400} \right]$$

$$\Rightarrow \log_{10} 100 = \frac{E_a}{2.303R} \left[\frac{400 - 300}{300 \times 400} \right]$$

$$\Rightarrow 2 = \frac{E_a \times 100}{2.303R(120000)}$$

$$\Rightarrow E_a = 2 \times 2.303 \times 8.31 \times 1200$$

$$\Rightarrow E_a = 45931.032 \text{ J/mol}$$

Therefore, the activation energy determined using the analytical method is **45931.032 J/mol**

RESULTS AND DISCUSSION

It is important to note that Arrhenius equation does not hold for complex reactions, high temperature reactions and simple photochemical reactions. Homogeneous reactions usually have higher activation energy and therefore, it is favoured at high temperature, whereas the heterogeneous reactions predominate at lower temperature. An Arrhenius equation is generally for gaseous equations.

The activation energy of a reaction can be both graphically and analytical determined if the rate of reactions and the corresponding temperatures of at least two set of conditions can be obtained. Though the activation energy determined through the graphical method (**47844.825J/mol**) and that which is determined through the analytic method (**45931.032J/mol**) should be the same but here the difference is **1,913.793J/mol**. This difference is as a result of using only two set of conditions. The accuracy increases as we have many different reaction rates and temperatures conditions.

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