# The Effect of Temperature and Acid Concentration on Corrosion of Low Carbon Steel in Hydrochloric Acid Media

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**Abstract: Problem statement:** The effect of different temperatures and acid concentrations on the corrosion of low carbon steel in hydrochloric acid were addressed in this study. **Approach:** The effect of temperature was explained by application of Arrhenius equation and transition state theory, while the acid concentration effect was explained using reaction kinetic equations. The combined effect of temperature and acid concentration then modeled using a nonlinear regression method. **Results:** A detail of thermodynamic parameters of activation (E, $\Delta H^*$ and $\Delta S^*$) and kinetic studies for the corrosion reaction were obtained. Nonlinear corrosion rates as a function of temperature and acid concentration equation were estimated with a good prediction corrosion rates values. **Conclusion:** The values of activation energy E and enthalpy of activation $\Delta H^*$ decrease with increase in acid concentration indicating the increasing in reaction rate. Entropy of activation $\Delta S^*$ tend to lower values with increasing in acid concentration which indicated that the activated complex was more orderly relative to the initial state. The corrosion reaction was approximately firs order reaction. The observed corrosion rate values from the experimental data were in a good agreement with that predicated by the mathematical equation.

**Key words:** Transition state theory, corrosion kinetic equation, activation parameters

## INTRODUCTION

Steel is one of the major construction materials, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions. Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of constructions. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations or in process solutions containing appreciable amount of hydrochloric acid. This acid is very corrosive to most of the common metals and alloys. Metals are exposed to the action of acids in many different ways and for many different reasons. Processes in which acids play a very important part are[1], Acids pickling, industrial acid cleaning and oil well acidizing in order to stimulate of oil well. One of the most commonly used acids in today's industrialized world is Hydrochloric acid HCl,

where some of its applications include chemical cleaning and processing, acid treatment of oil wells and other applications. The wide use of this acid has led to the concentration of this study on the corrosive effects of this acid on carbon steel, which is a versatile component in many industrial structures.

Activation parameters for some systems can be estimated either from an Arrhenius-type plot Eq. 1:

$$k = A \, \text{Exp}\left(-\frac{E}{R \, T}\right) \tag{1}$$

Where:
K = Reaction rate
A = Modified frequency factor (pre-exponential factor)
E = Activation energy (J mole$^{-1}$)
R = Gas constant (8.314 J mole$^{-1}$ K)
T = Absolute temperature (K), or from transition state theory[2]

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This theory shares certain similarities with collision theory, whereas reaction is postulated as occurring when molecules collide with or encounter each other. The basic assumption about the system that are made in transition state theory is that molecular system that have crossed the transition state in the direction of products can not turn around to form reactants. A transition state complex of relatively high energy is formed: The complex is then decays to products. The mathematical form of transition state theory may be written as:

$$k = \left(\frac{RT}{Nh}\right) \exp\left(-\left(\left(\frac{\Delta H^*}{RT}\right) + \left(\frac{\Delta S^*}{R}\right)\right)\right) \qquad (2)$$

$$k = \left(\frac{RT}{Nh}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \exp\left(\frac{\Delta S^*}{R}\right) \qquad (3)$$

Where:
$\Delta H^*$ = Enthalpy of activation
$\Delta S^*$ = Entropy of activation
N = Avogadr`s number ($6.022 \times 10^{23}$ molecule.$moL^{-1}$)
H = Plank's constant ($6.626 \times 10^{-34}$ J sec $moL^{-1}$)

A comparison of Eq. 3 with Arrhenius Equation the energy of activation E is related to the enthalpy of activation $\Delta H^*$. The pre-exponential factor (A) is now:

$$\left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^*}{R}\right)$$

With more complex reactants, when the simple collision theory fails, Eq. 3 is still satisfactory[3]. According to Grigorev et al.[4,5] and Antropove and Suvgira[6] that they apply the transition state theory on the corrosion of steel in acids, they stated that the rate-determining step for hydrogen evolution reaction is the recombination of adsorbed hydrogen to form hydrogen molecules. In acid-free, the Transition State of the rate determining recombination step represents a more orderly arrangement relative to the initial state and hence, negative value for the entropy of activation is obtained.

**Corrosion Reaction Kinetic:** Chemical kinetics is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

Corrosion reaction like almost all chemical reaction. Normally as the concentration of a corrosive acid media is increased, the corrosion rate is likewise increased. This is primarily due to the fact that the amounts of hydrogen ions, which are the active species, are increased, as acid concentration is increased[7].

Corrosion rate data as a function of acid concentration can be used to show the rate dependence of hydrochloric acid concentration. The first model proposed by Mathur and Vasudevan[8] are described by the following Eq. 4:

$$r = k e^{BC} \qquad (4)$$

Where:
k = The reaction rate constant
C = Acid concentration
B = Another constant for the reaction studies

This model can be compared with the conventional equation of chemical reaction kinetics:

$$r = k C^n \qquad (5)$$

where, n is the order of reaction. The aim of this study is to study the effect of temperature and acid concentration using Arrhenius Equation transition state equation and reaction rate kinetic equations on the corrosion of low carbon steel in HCl acid.

## MATERIALS AND METHODS

Specimens of area ($7.89 \times 1.5$ cm$^2$) and thicknesses of 0.09 cm of steel were used with small hole of about 1.0 mm diameter near the 1.5 cm side end for suspending. The specimens were first degreased with analar benzene and acetone and then annealed in a vacuum at 600°C for 1 h and cooled to room temperature. Samples were abraded in sequence under running tap water using emery paper of grad number 220, 320, 400 and 600 then washed with running tap water followed by distilled water, dried with clean tissue, immersed in acetone and benzene, kept in desiccators over silica gel bed until use. For these measurements the metal samples were completely immersed in 400cm$^3$ solution of HCl solution contained in 400 mL volume beakers. They were exposed for period of 2 h at desired temperature and normality of acid solution, than the metal samples were cleaned, washed with running tap water followed by distilled

water, dried, than immersed in benzene and acetone, dried again. The loss of a metal as a result of corrosion is then determined from the loss of masses in specimen. Mass loss values are usually recorded together with the exposed surface area of the specimen and the period of the test. Frequently the data are expressed as mass loss per unit time per unit area, g m$^{-2}$ day (gmd). In this research, the application of transition state theory and application of kinetic relationship for the corrosion reaction of low carbon steel in 1, 3 and 5 M HCl and at 30, 40, 50 and 60°C were studied. The steel specimens have the following chemical composition C 0.041 wt, Mn 0.311, P 0.05, S 0.007% and the remainder is iron.

## RESULTS

Table 1 shows 12 runs of weight loss experimental results of low carbon steel corrosion in 1, 3 and 5 M HCl acid solutions as function of temperature. As shown in Fig. 1, the corrosion rate increased with increasing in acid concentration and temperature.

Eq. 3 can be rearranged in the form of straight line equation in order to find the values of enthalpy and entropy of activations. The rearranged equation is:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \qquad (6)$$

Table 1: Effect of temperature and HCl acid concentration on the corrosion rate (g m$^{-2}$ day) of carbon steel

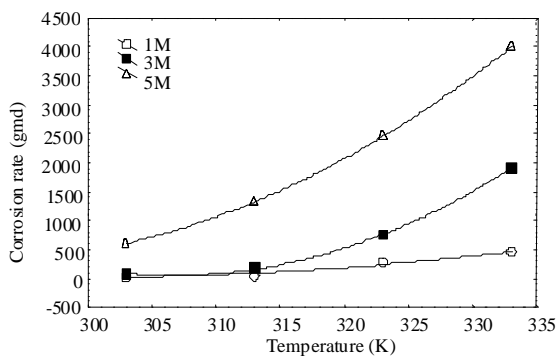| HCl conc. M | Temperature (°C) | | | |
|---|---|---|---|---|
| | 30 | 40 | 50 | 60 |
| 1 | 39.35 | 153.82 | 279.81 | 456.170 |
| 3 | 75.85 | 177.82 | 741.31 | 1905.460 |
| 5 | 602.55 | 1318.25 | 2454.71 | 3990.249 |



Fig. 1: Corrosion rate of low carbon steel as a function of temperature and acid concentration

Equation 6 can be draw as shown in Fig. 2 as, $\ln\left(\frac{K}{T}\right)$ Vs. $\left(\frac{1}{T}\right)$. The values of enthalpy of activation and entropy of activation can be evaluated from the slope and intercept. Table 2 shows these values at different conditions. The values of activation energies and frequency factors are evaluated using Eq. 1, by plotting:

$$\ln\left(\text{Corr.Rate}\right) \text{Vs.}\left(\frac{1}{T}\right)$$

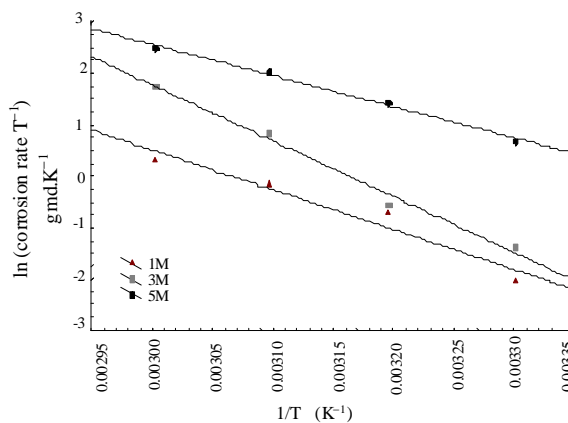as shown in Fig. 3 and these values are listed in Table 2 also.



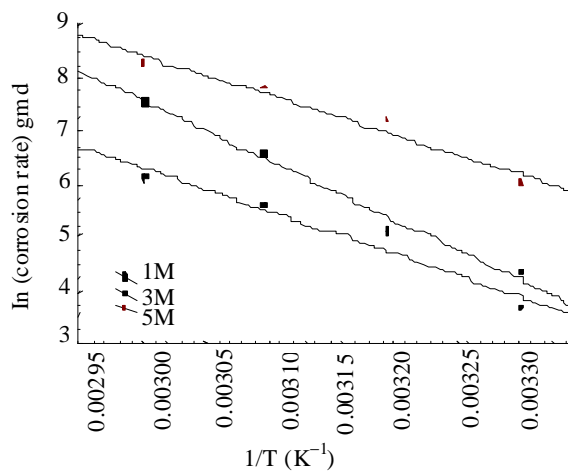Fig. 2: Transition state plot for the corrosion of low carbon



Fig. 3: Arrhunis plot for the corrosion of low carbon steel in HCL acid

Table 2: Values of enthalpy of activation, entropy of activation, activation energy and frequency factor at different acid concentrations

| Conc. M | Transition state equation | | | Arrhenius equation | | |
|---|---|---|---|---|---|---|
| | $\Delta H^*$ (kJ moL$^{-1}$) | $\Delta S^*$ (kJ moL$^{-1}$ K) | R | E(kJ mol$^{-1}$) | A(day$^{-1}$) | R |
| 1 | 90.708 | 0.008730 | 0.9443 | 70.12 | 45.7×10$^{12}$ | 0.9451 |
| 3 | 64.772 | 0.000542 | 0.9883 | 56.36 | 16.5×10$^{12}$ | 0.9885 |
| 5 | 50.494 | -0.02520 | 0.9693 | 52.94 | 8.40×10$^{12}$ | 0.9933 |
| Average value | 68.658 | -0.00531 | 0.9673 | 59.81 | 23.5×10$^{12}$ | 0.9756 |

## DISCUSSION

The values of $\Delta H^*$ was 90.708 (kJ moL$^{-1}$) at 1 M acid concentration. This value decrease with increasing in acid concentration, which indicate that the reaction need low energy to occur with increasing of acid concentration. This mean that the energy barrier of corrosion reaction decrease as the concentration of hydrochloric acid increase and activated complex or transition state complex can be formed faster with acid concentration increasing. The positive sign of $\Delta H^*$ reflects the endothermic nature of the steel dissolution process.

The values of $\Delta S^*$ were positive at 1 and 3 M acid concentration and tends to negative value at 5 M acid concentration. The corrosion of iron in acid solutions takes place with hydrogen depolarization. The spontaneous dissolution of iron can be described by anodic dissolution reaction $Fe = Fe^{++} + 2e$ accompanied by the corresponding cathodic reaction $2H^+ + 2e = H_2$[9]. According to Abiola[10], the corrosion of metals in neutral or acidic solution is cathodically controlled by the hydrogen evolution reaction which occur in two steps:

$$H^+ + e \rightarrow H_{ads} \qquad (7)$$

$$H^+ + H_{ads} \rightarrow H_2 \qquad (8)$$

The rate-determining step for the hydrogen evolution reaction is the recombination of adsorbed hydrogen atoms to form hydrogen molecules Eq. 8. At low concentration (1M) the transition state of the rate determining recombination step represent less orderly arrangement relative to initial state and hence a positive value for the entropy of activation was obtained. As acid concentration increased (3 M), the values of $\Delta S^*$ decreased, but it still positive. This may be due to the activated complex have some order than the initial state. Further increase in acid concentration (5 M), the entropy of activation has a negative value. These indicate that the activated complex is more orderly relative to the initial state.

From Eq. 1, it can be seen that at given temperature, the value of corrosion rate is jointly decided by the activation energy and pre-exponential factor. Values of E vary in the same way as the values of $\Delta H^*$. Activation energy decreased from 70.12 kJ moL$^{-1}$ at 1 M HCl-52.94 kJ moL$^{-1}$ at 5 M HCl. These values of E, approximately, agree with the literature data of E for iron and steel in hydrochloric acid which is ranged 58-100 kJ moL$^{-1}$[11-13]. Larabi et al.[14] found a value of activation energy of 60.5 kJ moL$^{-1}$ for the corrosion of mild steel in 1 M HCl. While, Chauhan et al.[14] who studied the corrosion of mild steel in different concentration of HCl acid solution, found that the value of E decreased form 48.06 kJ moL$^{-1}$ in 5 HCl-43.07 kJ moL$^{-1}$ in 15% HCl acid solution.

The kinetic constants can be obtained by rearranging Eq. 4 and 5, these equations can be rewrite in a line form:

$$\ln r = \ln k + BC \qquad (9)$$

By plotting ln r Vs C, as shown in Fig. 4, the values of B and k can be obtained from the slopes and intercepts of these lines. The second kinetic equation can be written as:

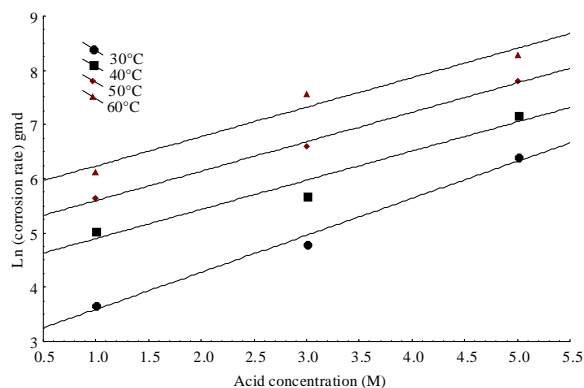$$\ln r = \ln k + n \ln C \qquad (10)$$



Fig. 4: Rate equation as a function of acid concentration at different temperatures

Table 3: Kinetics parameters of the first model and second conventional reaction model

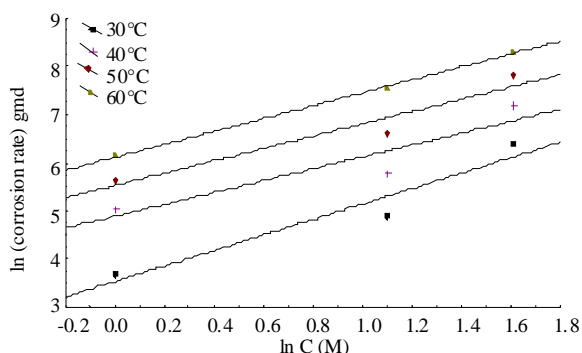| T(°C) | First model (Eq. 4) | | | Second model (Eq. 5) | | |
|---|---|---|---|---|---|---|
| | k(gmd) | B(gmd.N⁻¹) | R | k (g md) | n | R |
| 30 | 15.6990 | 0.582 | 0.9979 | 22.799 | 1.521 | 0.9962 |
| 40 | 65.9040 | 0.538 | 0.9912 | 95.610 | 1.144 | 0.9869 |
| 50 | 156.6470 | 0.543 | 0.9995 | 188.420 | 1.275 | 0.9910 |
| 60 | 297.2870 | 0.542 | 0.9911 | 352.105 | 1.341 | 0.9987 |
| Average value | 133.8843 | 0.551 | 0.9949 | 164.733 | 1.320 | 0.9932 |



Fig. 5: Conventional chemical reaction rate as function of acid concentration at different temperature

And can be drawn as shown in Fig. 5. The values of n and k can also be obtained from the slopes and intercepts of these lines. Table 3 shows these values of kinetic parameters. The values of correlation coefficients also listed to show the relation between the variables, these values obtained using statistical software program[15].

The changes in temperature have great effect when the rate-determining step is the activation process. In general if the diffusion rates are doubled for a certain increase in temperature, activation process may be increased by 10-100 times depending on the magnitude of the activation energy.

The values of rate constants k, increased with increasing in temperature and this observed from both models. Jianguo *et al.*[16], who study the corrosion of low carbon steel in acid media at different concentrations. The value of slope B is constant up to 1.5 M acid concentration and then it reduced to a lower value for acid concentration grater than 1.5 M. The change in slope (value of B) may be due to the formation of a tightly adsorbed more protective corrosion products layer on metal surface at high acid concentration[8]. In this study, the values of B approximately constant with temperature changes, with average value of 0.551 and it is constant through acid concentration range, indicating that the mechanism of corrosion reaction is the same at different acid concentrations. The values of n, which obtained from the conventional kinetic equation, were around unity which indicates that the reaction approximately of first order. The first model was more suitable to represent the corrosion reaction process of low carbon steel in HCl acid, with higher values of correlation coefficients (R), as compared with the values obtained with second model, this is due to high increase in corrosion rate with acid concentration increasing, so that the exponential representation of the corrosion rate data is better than the linear one.

Mathur[8] state that the conventional rate Eq. 5 differs from the present rate Eq. 4 in the concentration term. If BC<<1, the exponential term ($e^{BC}$) can be expanded and Eq. 4 can be written as:

$$r = k(1 + BC) \tag{11}$$

Relation (9) indicates that r varies linearly with concentration C only in very low concentration of electrolytes solutions, as in conventional rate Eq. 5. Hence, Eq. 5 is only special case of the more general Eq. 4. Also, Eq. 4 appears to be more valid than the linear rate Eq. 5 at high acids concentration.

**Combined influence of temperature and acid concentration:** The combined effect of temperature and acid concentration on the corrosion of low carbon steel in hydrochloric acid can be evaluated using Arrhenius equation Eq. 1 and 4, since both equations were more suitable in representing the corrosion rate data than transition state theory Eq. 3 and conventional Eq. of chemical reaction Eq. 5 depending on the values of correlation coefficients. Therefore, the combined equation can be obtained by substituting Eq. 1 in 4, so that:

$$r = A \exp(-\frac{E}{RT}) \exp(BC) \tag{12}$$

The values of A, E and B were defined previously: These values can be non-linearly estimated using Levenberg-Marquardt estimation method[15]. Equation 11 was suitable in representing the effect of temperature and acid concentration on the corrosion rates with a

correlation coefficient of 0.9907. The estimated equation can be written in the form of:

$$r = 69.1 \times 10^{12} \exp(-\frac{6340}{T}) \exp(0.48C) \qquad (13)$$

The coefficient $69.1 \times 10^{12}$ which appears in Eq. 13 was in the same order of frequency factor values which shown in Table 2, with average value of $23.5 \times 10^{12}$. Acid concentration coefficient, of value equal to 0.48, was in a good agreement with the values of B shown in Table 3, with average B values equal to 0.55. Temperature coefficient of value $\left(\frac{E}{R} = 6340K^{-1}, E = 52.7\frac{kJ}{mol}\right)$ was in agreement with the average values of the slope of Arrhenius Equation $\left(\frac{E}{R} = 7193.5K^{-1}, E = 59.81\frac{kJ}{mol}\right)$ shown in Table 2.

The observed corrosion rate data from the experiments and the predicted corrosion rate data by Eq. 11 are shown in Fig. 6, with a line slope of 1.03, indicating a good correlation between the two values.

Wang *et al.*[17] and Morad[18] use Arrhenius equation and Eq. 4 separately to evaluate the kinetic parameter for the corrosion of carbon steel in acid graphically, in which he obtained the value of k and B from the plot of ln r against C and the values E and A were calculated from a plot of ln r against $\frac{1}{T}$, while in our combination model, these parameters can be calculated using Eq. 11.

Ehteram and Al-Moubaraki[19] studied the corrosion behavior of mild steel in hydrochloric acid solutions. They correlated relation between the corrosion rate r with the acid concentration by the following equation (log r = log k + B log C) and they conclude that the studied mild steel corrodes in HCl solutions with a first order reaction and the corrosion rate increases with the increase in acid concentration, with good correlation coefficient of 0.969. The estimated B and k values are 0.56 and $2.07 \times 10^{-6}$ moL cm$^{-2}$ min$^{-1}$, respectively, which is in a good agreement with the obtained results.

Kinetic analysis of combined effect of temperature and acid concentration may by very useful in understanding the mechanism of corrosion reaction. James *et al.*[20], depending on the values of temperature and acid concentration, stated that the corrosion of steel in uninhibited hydrochloric acid solution is a heterogeneous one, composed of anodic and cathodic reaction.
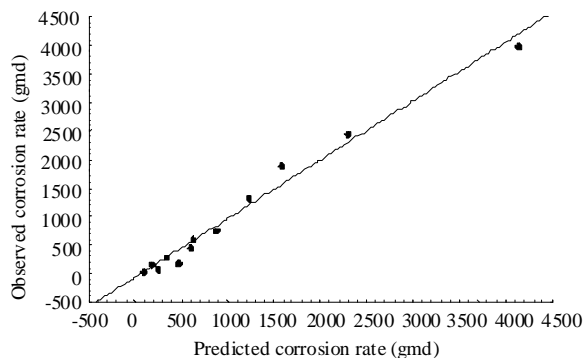


Fig. 6: Observed Vs predicted corrosion rates of low carbon steel in HCL acid obtained using combined influence equation

## CONCLUSION

Both Arrhenius equation and transition state theory were suitable to represent the effect of temperature on the corrosion rates of steel in aqueous HCl acid. Present rate equation which used in this study was more suitable than the conventional equation of chemical reaction. The combined temperature and acid concentration model was estimated using nonlinear estimation method, this model was suitable to represent the combined effect on corrosion rate data of low carbon steel in hydrochloric acid.

## ACKNOWLEDGMENT

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