Transition State Theory and Reaction Kinetic for the Corrosion of Steel in Acid Media

Dr. Anees Abdullah
Daiyla University
College of Engineering
aneesdr@yahoo.com

Dr. Khalid Whaleed Hameed
Baghdad University
College of Engineering
kwhameed@yahoo.com

Abstract:

The application of transition state theory and reaction kinetic equations were applied on the corrosion of low carbon steel in hydrochloric acid at different temperature and different acid concentration. The values of enthalpy of activation, entropy of activations, and other kinetics parameters of corrosion reaction were obtained. Enthalpy of activation increased with decrease of acid concentration, while the values of entropy of activation decrease with acid concentration increase.

Key words: Transition state theory, Corrosion kinetic equation, Activation parameters, Low carbon steel.

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1. Introduction:

Activation parameters for some systems can be calculated from an Arrhenius-type plot equation (1).

$$Corrosion \ Rate \ (C.R.) = A \ Exp\left(-\frac{E}{R\,T}\right) \qquad \ldots(1)$$

Where:

A = Modified Frequency factor (pre-exponential factor)
E = Activation energy (J/mole)
R = Gas constant (8.314 J/mole.K)
　　　　　　T = Absolute temperature (K)

or from transition state theory [1]; this theory shares certain similarities with collision theory. 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 reaction coordinates diagram describes energy changes during the course of reaction, and we can see that the starting materials and products lie at energy minima and are separated an energy barrier, the maximum of which is called *transition state*. If the transition state is too high in energy, it will not be accessible under normal conditions and no reaction will occur. This is pictured schematically in (Fig.1) for general reaction;

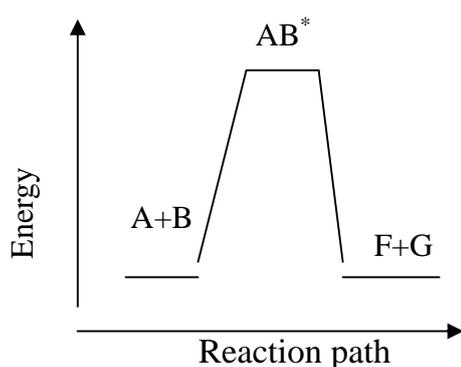$$A+B \rightarrow F+G \qquad\qquad (2)$$

Fig.(1) Formation of Activated Complex [1].

In this research, the application of transition state theory and application of kinetic relationship for the corrosion reaction of steel in acid media. This study applied on the corrosion rate data of Safa [2]. Safa studied the corrosion of low carbon steel in 1,3, and 5 N HCl, and at 30, 40, 50, and 60 ^{o}C.

2. Transition State Derivation:

AB^{*} is the activated complex or transition state complex. The reaction coordinate simply depicts the progress of reaction from reactants to wards products via the transition state complex.

Transition state complex is postulated to be in equilibrium with reactant: -

$$A + B \leftrightarrow AB^* \qquad \ldots (3)$$

$$K^* = \frac{[AB^*]}{[A][B]} \qquad \ldots (4)$$
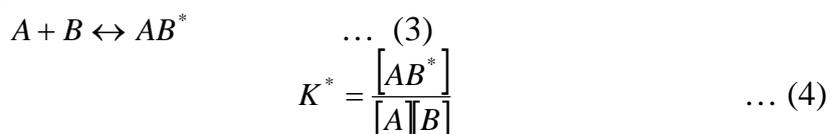
Where K^* is equilibrium constant. Further the rate of reaction is postulated to depend only on the rate of decay of AB^* to products;

$$A + B \xleftrightarrow[K_2]{K_1} AB^* \xrightarrow{K_3} F + G \qquad \ldots (5)$$
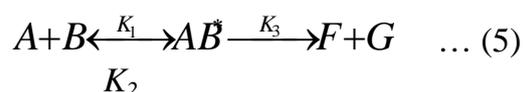
The rate reaction (r) is then;

$$r = K_3 [AB^*] \qquad \ldots (6)$$

From equation (4) the concentration of AB^* can be obtained;

$$r = K_3 K^* [A][B] \qquad \ldots (7)$$

And

$$r = K[A][B] \qquad \ldots (8)$$

Where

$$K = K_3 K^* \qquad \ldots (9)$$

Statistical mechanical consideration predicts that the state complex will decay with a rate constant [3];

$$K_3 = \frac{RT}{Nh} \qquad \ldots (10)$$

Where:

R: the gas constant (8.314 J.K^{-1}.mol^{-1})

N: Avogadr`s number (6.022 x 10^{23} molecule.mol^{-1})

h: Plank`s constant (6.626 x10^{-34} J.s.molecule^{-1})

So equation (9) will be;

$$K = \left(\frac{RT}{Nh}\right) K^* \qquad \ldots (11)$$

From thermodynamics;

$$\Delta G = -RT \ln K \qquad \ldots (12)$$

So, the standard free energy of activation for the process $A + B \rightarrow AB^*$ is;

$$\Delta G^* = -RT \ln K^* \qquad \ldots (12a)$$

And

3

$$K^* = \exp\left(\frac{-\Delta G^*}{RT}\right) \qquad \text{...(12b)}$$

And from equation (11), $K = \left(\dfrac{RT}{Nh}\right)\exp\left(-\dfrac{\Delta G^*}{RT}\right)$ ...(13)

Again, from thermodynamic the relation of free energy to enthalpy and entropy is;

$\Delta G = \Delta H - T\Delta S$ …(14)

So, equation (13) may be written as;

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

$$K = \left(\frac{RT}{Nh}\right)\exp\left(-\frac{\Delta H^*}{RT}\right)\exp\left(\frac{\Delta S^*}{R}\right) \qquad …(15)$$

A comparison of equation (15) with Arrhnius equation, the energy of activation E is related to the enthalpy of activation ΔH^*. The pre-exponential factor (A) is now $\left(\dfrac{RT}{Nh}\right)\exp\left(\dfrac{\Delta S^*}{R}\right)$. The entropy of activation will be negative for the reaction of the type $A + B \rightarrow AB^* \rightarrow P$, Since AB^* is definitely more organized then A and B. For process of type $AB \rightarrow AB^* \rightarrow A + B$ the entropy of activation will generally be positive, since activated complex will most likely have acquired some of the disorder which will eventually result in total break down into A and B. With more complex reactants, when the simple collision theory fails, equation (15) is still satisfactory [4] .

According to Grigorev et al [5,6] and Antropove and Suvgira [7] that they apply the transition state theory on the corrosion of steel in acids, they stated that the rate-determining steps 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.

3. Corrosion Reaction Kinetic:

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 [8].

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 [9] and was used here is:

$$r = ke^{BC} \qquad \dots (16)$$

Where k is the reaction rate constant and *B* is another constant for the reaction studies. This model can be compared with the conventional equation of chemical reaction kinetics:

$$r = kC^n \qquad \dots (17)$$

Where *n* is the order of reaction.

4. Results and Discussions:

Equation (15) 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:

$$\ln\left(\frac{K}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \dots (18)$$

Equation (18) can be draw as shown in figure (2) as, $\ln\left(\frac{K}{T}\right) vs.\left(\frac{1}{T}\right)$,

and from the slope and intercept the values of enthalpy of activation and entropy of activation can be evaluated. Table (1) shows these values at different conditions.
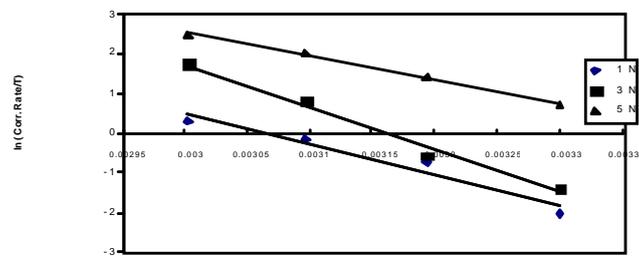

Fig 2 ln K /T as a function of 1/T for the corrosion of low carbon steel at different HCl concentrations

5

Table (1) Enthalpy of activation and entropy of activation at different acid concentrations.

Conc. N	ΔH^* (kJ/mol)	ΔS^* (kJ/mol.K)
1	90.708	0.00873
3	64.772	0.000542
5	50.494	-0.02520

The values of ΔH^* was 90.708 (kJ/mol) at 1 N 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 values of ΔS^* were positive at 1 and 3 N acid concentration, and tends to negative value at 5 N acid concentration. According to Pavor and Kier [10], the corrosion of metals in neutral or acidic solution is cathodically controlled by the hydrogen evolution reaction which occur in two steps,

$$H^+ + e \rightarrow H_{ads} \ldots (19)$$

$$H^+ + H_{ads} \rightarrow H_2 \quad \ldots (20)$$
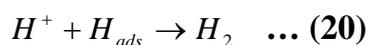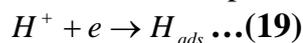
The rate-determining step for the hydrogen evolution reaction is the recombination of adsorbed hydrogen atoms to form hydrogen molecules (equation 20). At low concentration (1N) the transition state of the rate determining recombination step represent less orderly arrangement relative to initial state and hence a positive value for the entropy of activation was obtained. As acid concentration increased (3N), the values of ΔS^* decreased, but it still positive. This may be to that the activated complex have some order than the initial state. Further increase in acid concentration (5N), the entropy of activation has a negative value. This indicate that the activated complex is more orderly relative to the initial state.

Kinetic constants can be obtained by rearranging equation (16) and equation (17), these equations can be rewrite as:

$$\ln r = \ln k + BC \qquad \ldots (16a)$$

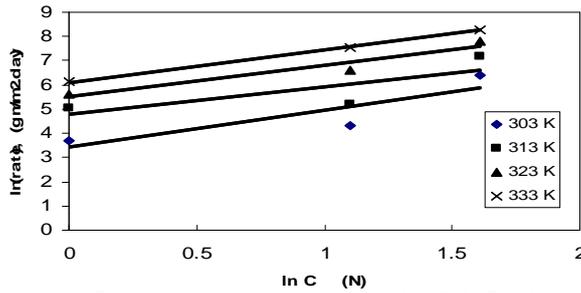And can be drawn as *ln r vs. C*, as shown in figure (3).

Fig. 3 Conventional Chemical Reaction Rate Equation as a Function of Acid Concentration at Different Temperatures

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:

$$\ln r = \ln k + n \ln C \qquad \dots (17a)$$
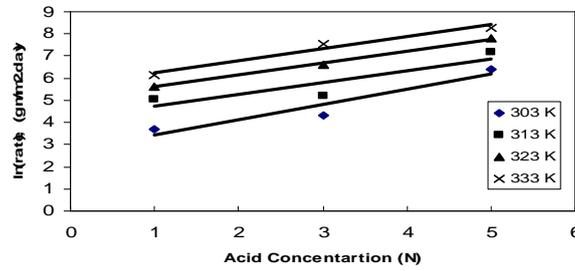
And can be drawn as shown in figure (4).

Fig. 4 Rate of reaction as a function of acid concentration

The values of n and k can also be obtained from the slopes and intercepts of these lines. Table (2) summarized these values of kinetic parameters.

Table (2) Kinetics parameters of the first model and second conventional reaction model.

First model			
T (^{o}C)	k	B	R
30	15.699	0.582	0.9979
40	65.904	0.538	0.9912
50	156.647	0.543	0.9995
60	297.287	0.5424	0.9911
Second model			
T (^{o}C)	k	n	R
30	30.799	1.521	0.9962
40	117.610	1.144	0.9869
50	252.420	1.275	0.9910
60	451.105	1.341	0.9987

7

The values of correlation coefficients also listed to show the relation between the variables, these values obtained using Statistical Software Program [11].

Temperature changes have the greatest 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 the both models. The values of B approximately constant with average value of about (0.551). the values of n, which obtained from the conventional kinetic equation were around unity which indicate 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, because of the higher values of correlation coefficients (R), as compared with the values obtained with second model. The average values of correlation coefficients for the first model was (0.995), while these values were lower for the second model (0.992).

Mathur [9] state that the conventional rate equation (17) differs from the present rate equation (16) in the concentration term. If *BC<<1*, the exponential term (e^{BC}) can be expanded and equation (16) can be written as:

$$r = k(1 + BC) \qquad \dots (19)$$

Relation (19) indicates that r varies linearly with concentration C only in very low concentration of electrolytes solutions, as in conventional rate equation (17). Hence, equation (17) is only special case of the more general equation (16). Also, equation (16) appears to be more valid than the linear rate equation (17) at high acids concentration.

5. Conclusion:

The values of enthalpy of activation and entropy of activation were obtained using transition state theory. Enthalpy of activation increased with decrease of acid concentration, indicating that the corrosion reaction process increase as acid concentration increase. The values of entropy of activation decrease with acid concentration increase indicating that the activated complex formed has some degree of disorder with rising in acid concentration.

Present rate equation which used in this study was more suitable than the conventional equation of chemical reaction.

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9