

Heat of Activation in Electrode Kinetics

The Fe/Fe⁺⁺.aq Electrode

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The treatment of data on the effect of temperature on the rate of electrode reactions is considered, and a way is shown in which the standard heat of activation (ΔH_o^*) of symmetric electrode reactions may be determined. The method is applied to the Fe/Fe⁺⁺.aq electrode reactions, for which the available data indicate:

$$\Delta H_o^* \text{ (anodic)} = 2 \text{ kcal(H-scale)}$$

$$\Delta H_o^* \text{ (cathodic)} = 44 \text{ kcal(H-scale)}$$

The accuracy and the meaning of these values are somewhat discussed.

1.0 INTRODUCTION

There seems at present to be some confusion as to the determination of the energy or heat of activation of electrode reactions. The so far most commonly accepted ways of determining such an energy are based on the equations:

$$Q_V = -2.303 R (\text{dlog } i/\text{d}(1/T))_V \quad (1)$$

$$Q_o = -2.303 R (\text{dlog } i_o/\text{d}(1/T)) \quad (2)$$

where i_o is the exchange current of the electrode reaction considered, and Q_V and Q_o are called the Arrhenius energy of activation at the potential V and at the reversible potential, respectively.

Bockris¹ has clearly shown that these quantities are not »true» energies or heats of activation, but that they also include other terms, the main of which is proportional to the change in standard heat content for the overall electrode reaction. He therefore has suggested that Q_o be termed »the virtual heat of activation at the reversible potential». This quantity is common for two mutually reverse reactions. The application of (1) and (2) includes moreover the often inadequate assumption that the reactant activities are temperature independent. Eqn. (2) even implies that the activities of the reaction products also are independent of temperature.

Some investigators have improved (2) by putting i_0/T into it instead of merely i_0 . This certainly brings the equation in better agreement with the absolute rate theory². However, it does not alter the fact that the quantity determined is not a true heat of activation, and that it therefore is of minor use in revealing the properties of the activated state.

The quantity that would serve best in this respect, is the *standard heat of activation*, as this would give the best basis for comparison with other often well known standard energies connected with the reaction system (e.g. heat of reaction, heat of formation, heat of sublimation, etc.). Because of the apparent inaccessibility of single electrode potentials, the standard heat of activation of an electrode reaction may at present seem difficult to determine¹. In the present paper, however, a way is suggested that should be applicable to symmetric reactions. The method is moreover applied to determine the standard heat of activation of the reactions of the Fe/Fe⁺⁺aq electrode from experimental data previously obtained by Hoar and Hurlen³.

2.0 THEORETICAL DEDUCTIONS

The standard heat of activation (ΔH_0^*) for any reaction is defined as the change in standard heat content of the reaction system when going from its initial to its activated state:

$$\Delta H_0^* = H_0^* - H_0^{(i)} \quad (3)$$

Quite analogous definitions apply to the standard energy and the standard entropy of activation. All these definitions, however, imply that the initial state should encompass just as many moles of the reactants as there are molecules (or atoms or ions) reacting for each act of the rate determining step. This is not necessarily equal to what is indicated by the equation for the overall reaction considered, but depends on the number of times (ν) the rate determining step occurs when the overall reaction occurs once. Thus, if we choose to define the initial state in the ordinary thermodynamic way (which certainly is the best in order to avoid confusion), (3) must be rewritten in the form:

$$\Delta H_0^* = H_0^* - \frac{1}{\nu} H_0^i \quad (4)$$

From (4), it is further seen that the standard heat of activation of a reaction should be related to that of its reverse reaction and to the ordinary standard heat of reaction by the following equation:

$$\Delta \vec{H}_0^* - \Delta \overleftarrow{H}_0^* = \frac{1}{\nu} \Delta \vec{H}_0 \quad (5)$$

In the modern theory of electrode kinetics^{1,4}, the standard exchange current (J_0) of a reaction system is given by an Arrhenius equation of the following type:

$$\log (J_0/T) = C - \frac{cnF \Delta \phi_0}{2.303\nu RT} - \frac{\Delta H_0^*}{2.303RT} \quad (6)$$

J_o is defined by

$$J_o = i_o [(IIa)_r^{1-\alpha}(IIa)_p^\alpha]^{-1/\nu} \quad (7)$$

where i_o is the exchange current at the activity products $(IIa)_r$ and $(IIa)_p$ of the reactants and the reaction products, respectively, (each activity counting as many times as given by the respective stoichiometric factors in the overall reaction). α is the apparent symmetry factor (equal to $\beta + \gamma$ in Refs. 1, 4). ν is the number of electrons consumed during one act of the overall reaction (positive for cathodic and negative for anodic reactions). $\Delta \theta_o$ is the Galvani potential difference between electrode and solution ($\theta_M - \theta_{sl}$) at the standard potential of the reaction system. C consists mainly of temperature independent constants and includes moreover the standard entropy of activation and the activity coefficient of the activated complex (both of which will here be assumed independent of temperature). The presumably small energy term δ introduced by Parsons ⁴ to represent the possible potential independent part of the electrical contribution to the standard free energy required to transform the system from the two end states (initial and final) to the two states nearest to the activated state (one on each side), may here be regarded either as neglected or as included in the standard heat of activation. It seems so far quite impossible to separate these two energy terms experimentally.

If $\Delta \theta_o$ and its temperature dependence were known, the standard heat of activation of a reaction could have been determined through the relationship (6), but it is well recognized that we so far are unable to determine the Galvani potential difference between two phases. In the case of symmetric reactions, however, we can easily manage without this knowledge. Such reactions are characterized by

$$\alpha = 1/2 \quad (8)$$

For two mutually reverse reactions of this type, the term containing $\Delta \theta_o$ in (6) will be equal in magnitude, but opposite in sign, whereby this term will cancel out in the sum of the heats of activation of these two reactions. We thus have from (6) and (8):

$$2 \log(J_o/T) = \vec{C} + \overleftarrow{C} - \frac{\Delta \vec{H}_o^* + \Delta \overleftarrow{H}_o^*}{2.303 RT} \quad (9)$$

By differentiating (9) with respect to $1/T$ and combining with (5), we further have:

$$\Delta H_o^* = -2.303 R \frac{d \log(J_o/T)}{d(1/T)} + \frac{1}{2\nu} \Delta H_o \quad (10)$$

From this relationship, we should be able to determine the standard heat of activation of any single electrode reaction for which (8) is valid. However, if hydrogen scale values of ΔH_o are used, ΔH_o^* will also be referred to this arbitrary scale.

3.0 APPLICATION TO THE Fe/Fe⁺⁺aq ELECTRODE

In a previous work⁵, it has been shown that we for the Fe/Fe⁺⁺aq electrode reactions have:

$$\alpha = \frac{1}{2} \quad (11a)$$

$$\nu = \frac{1}{2} \quad (11b)$$

$$n_a = -2 \quad (11c)$$

$$n_c = +2 \quad (11d)$$

$$(IIa)_a = a_{\text{OH}^-}^{1/2} \quad (11e)$$

$$(IIa)_c = a_{\text{Fe}^{++}} \cdot a_{\text{OH}^-}^{1/2} \quad (11f)$$

where the indexes a and c refer to the anodic and the cathodic reaction, respectively. As (11a) is in accordance with (8), the heats of activation of these reactions should be in accordance with (10).

Values obtained by Hoar and Hurlen³ for the exchange current (i_0) of the Fe/Fe⁺⁺aq electrode in a solution of 0.05 M FeSO₄ + 0.1 M NaHSO₄ at 0, 25, and 50°C are quoted in Table 1. This table also gives data for the pH of the solutions, for the dissociation constant of water, and for the values thereby obtained for pOH at the three temperatures concerned.

There does not seem to be any direct data available on the effect of temperature on the ferrous ion activity. In this treatment, therefore, we shall assume this effect to be negligible and the ferrous ion activity coefficient to be the same as in a pure ferrous sulphate solution of the same ionic strength. The actual ionic strength is about 0.4 which corresponds to that of 0.1 M FeSO₄. From the activity coefficient data given by Robinson and Stokes⁷ for similar divalent metal sulphates, we thus have $\gamma_{\text{FeSO}_4} = 0.15$. By further assuming the relationship $\gamma_{\text{Fe}^{++}} = \gamma_{\text{SO}_4^{--}} = \gamma_{\text{FeSO}_4}$ to be sufficiently valid, the ferrous ion activity should be as given in Table 1.

From the data in Table 1 and eqns. (11), values have been calculated for the quantity J_0 defined by (7). These values are given in Table 2.

In Fig. 1, $\log(J_0/T)$ is plotted against $1/T$, and the line drawn in this diagram, corresponds to:

$$-2.303 R \frac{d \log (J_0/T)}{d(1/T)} = 23.0 \text{ kcal} \quad (12)$$

Less attention is thereby paid to the data at 50°C than to those at 25 and 0°C. Both the potential measurements and the pH measurements by which the data have been obtained, have namely been carried out with quinhydrone electrodes, and it is well known that such a reference electrode is less reliable at higher temperatures. Strictly, it is not recommended⁸ for use at temperatures above 38°C.

The accepted value for the standard heat of reaction of the iron electrode is⁹:

$$\Delta H_{o,a} = -\Delta H_{o,c} = -21.0 \text{ kcal (H-scale)} \quad (13)$$

Table 1. Data for Fe/Fe⁺⁺+aq and activities in 0.05 M FeSO₄ + 0.1 M NaHSO₄ at various temperatures

Temperature (°C)	0	25	50
Exchange current ^a (A/cm ²)	3.9×10^{-14}	2.5×10^{-11}	1.2×10^{-9}
pH (Ref. ^{sb})	1.317	1.474	1.615
pK _w (Ref. ^c)	14.944	13.997	13.262
pOH (see text)	13.627	12.523	11.647
$\alpha_{\text{Fe}^{++}}$ (see text)	(0.0075)	0.0075	(0.0075)

Table 2. Calculated values of J_0 (defined by (7)) at various temperatures

T (°C)	0	25	50
log J_0 (A/cm ²)	2.343	4.046	4.851
log (J_0/T)	-0.093	1.572	2.342

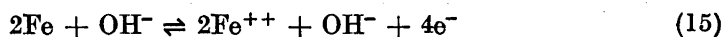
From (10), (11b), (12), and (13), we then have for the standard heats of activation of the iron electrode reactions:

$$\Delta H_{o,a}^* = 2 \text{ kcal (H-scale)} \quad (14a)$$

$$\Delta H_{o,c}^* = 44 \text{ kcal (H-scale)} \quad (14b)$$

As these values are based on measurements at three different temperatures only, and the data for one of these temperatures probably are less reliable, they cannot be regarded very much accurate. It is not likely, however, that they should be more than 1-2 kcal wrong in either direction. The data obtained at 50°C may further possibly indicate that they are rather too high than too low.

It has previously⁵ been shown that the kinetic unit reactions (the reaction occurring for each act of the rate determining step) of the Fe/Fe⁺⁺+aq electrode are represented by:



This means that the heats of activation refer to the transfer of two gram-atoms iron and one gramatom hydroxyl ions from the initial to the activated state. Thus, if one should like to express these heats as energy per gramatom iron, the values obtained must be divided by two.

Even though the present results are based on rather meager experimental data, it seems justified to conclude that the standard enthalpy of the activated state of the Fe/Fe⁺⁺+aq electrode is not much higher than that of the reduced

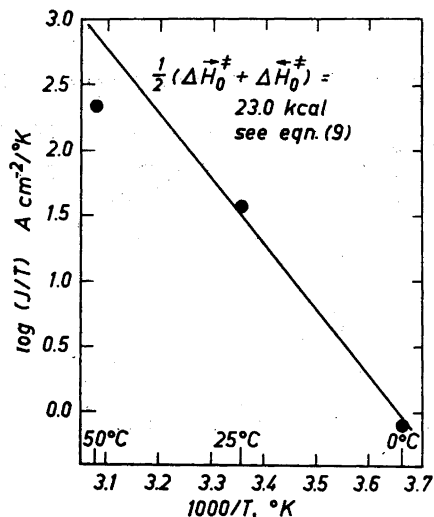


Fig. 1. Arrhenius plot for the standard exchange current of the Fe/Fe⁺⁺aq electrode.

state (the initial state of the anodic reaction) of this electrode. It should have been interesting to compare the iron electrode with other metal/metal-ion electrodes in this respect. As far as we know, however, this is the very first determination of the standard heat of activation of any such electrode reaction, and further work is therefore needed before a comparison can be made.

4.0 DISCUSSION

In the well known monograph by Bockris¹ on electrode kinetics, it is stated that «little interest attaches to the evaluation of the standard heats of activation of electrode reactions because the potentials to which they refer cannot be experimentally determined». In this connection, Bockris also refers to a work of Temkin¹⁰. To the author, however, this statement seems rather strange. The standard heat of activation is namely a pure chemical term that is independent of the potential in just the same way as the standard heat of reaction. It should therefore be no more need of referring the one than the other of these quantities to any special potential.

Another problem is that the standard heat of activation may be difficult to determine because of the inaccessibility of single electrode potentials (see eqn. (6)). In the present paper, however, it has been shown that this problem is easily eliminated in the case of symmetric reactions ($\alpha = 1/2$). As most electrode systems appear to be symmetric (or nearly symmetric), the way here suggested for the determination of standard heats of activation might have a rather wide applicability.

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