

Heats of Activation of the Cu/Cu_{aq}⁺⁺ Electrode

TOR HURLEN

Central Institute for Industrial Research, Blindern, Oslo, Norway

From measurements of the effect of temperature (0–45°C) on the anodic polarization of copper in 0.1 N sulphuric acid and from known data on the temperature coefficient of the standard potential of this metal, a mean standard heat of activation of:

$$\Delta H_0^*(\text{mean}) = 15.2 \text{ kcal}$$

has been found for the Cu/Cu_{aq}⁺⁺ electrode. On the basis of the kinetic stoichiometry and the heat of reaction of this electrode, this has been shown to indicate:

$$\Delta H_0^*(\text{anodic}) = 30.6 \text{ kcal (H-scale)}$$

$$\Delta H_0^*(\text{cathodic}) = -0.2 \text{ kcal (H-scale)}$$

The results further give an apparent Arrhenius factor of approximately:

$$A = 35 nFT/\nu \text{ A/cm}^2$$

These values are compared with corresponding values for the Fe/Fe_{aq}⁺⁺ electrode, and their accuracy and meaning are discussed.

The measurements support previous results in showing a Tafel slope of $2.303RT/2F$ for the anodic copper dissolution reaction under stationary conditions.

1.0 INTRODUCTION

In a previous work¹ on copper in acidified cupric sulphate solutions at 20 and 25°C, it has been shown that the Cu/Cu_{aq}⁺⁺ electrode is symmetric and that its kinetic unit reaction^{1,2} is:



It has further been shown¹ that the absolute rate of anodic dissolution of copper in 0.1 N sulphuric acid is not measurably affected by the addition of cupric sulphate to this electrolyte (the highest concentration tried being 0.3 M). Thereby, the standard exchange current (J_0) of the Cu/Cu_{aq}⁺⁺ electrode in these solutions is given by its anodic polarization curve in 0.1 N sulphuric acid and its standard potential.

In the present work, advantage has been made of these findings in determining the heat of activation of the copper electrode reactions from measurements of the effect of temperature (0, 15, 35, and 45°C) on the *anodic* polarization curve in 0.1 N sulphuric acid and from known data on the effect of temperature on the standard potential of copper³. No corrections need here to be made for changes in the sulphuric acid activity and the water dissociation constant with temperature, as neither the sulphate (nor bisulphate) activity nor the pH have been found to affect the dissolution reaction very much¹.

Previous determinations⁴⁻⁶ have invariably been made from *cathodic* overvoltage measurements at various temperatures in acidified cupric sulphate solutions of given composition. Seiter and Fischer⁴ thereby obtained:

$$-R \, d(\ln i_o)/d(1/T) = 12.3 \pm 2.0 \text{ kcal}$$

for the temperature effect (10–55°C) on the exchange current (i_o) in 1 N cupric sulphate + 1 N sulphuric acid. The results of Barnes, Storey, and Pick⁵ (same electrolyte composition at 20–40°C) indicate a higher value (not explicitly given, but apparently 15–20 kcal) for the same relationship, whereas Mattsson and Lindström⁶ report a corresponding value of 9.2 kcal. All these values, however, may include a possible effect of temperature on the cupric sulphate activity in the solutions applied (see eqns. (3) and (4) below). Such an effect is not encountered in the determinations made in the present work.

2.0 THEORETICAL BASIS

It has previously⁷ been shown that the mean standard heat of activation of two mutually reverse and *symmetric* electrode reactions is given by

$$\Delta H_o^* \text{ (mean)} = -R \, d \ln(J_o/T)/d(1/T) \quad (2)$$

provided the pre-exponential factor (including the exponential activation entropy term) in the transition state equation for their rate constants is directly proportional to the Kelvin temperature. The mean standard heat of activation for symmetric reactions is defined by:

$$\Delta H_o^* \text{ (mean)} = \frac{1}{2} (\Delta H_{o,a}^* + \Delta H_{o,c}^*) \quad (3)$$

where the subscripts a and c refer to the anodic and the reverse cathodic reaction, respectively. The standard exchange current (J_o) is defined by:

$$J_o = i_o [(IIa)_r]^{1-a} [(IIa)_p]^a \quad (4)$$

where i_o is the exchange current at the activity products $(IIa)_r$ and $(IIa)_p$ of the reactants and reaction products according to the kinetic unit equation (eqn.(1) in the present case), and a is the symmetry factor for the reaction from reactants to products. It is thus of no consequence in which direction a reaction is being considered to occur.

It has further been shown⁷ that the standard heat of activation of any one symmetric electrode reaction for thermodynamic reasons must be given by:

$$\Delta H_o^* = \Delta H_o^* \text{ (mean)} + \frac{1}{2} (\Delta H_o/\nu) \quad (5)$$

where ΔH_o is the standard heat of reaction and ν the stoichiometric number

of the reaction in question. The standard heat of reaction is here being referred to one "mole" of the thermodynamic overall reaction (in the present case: $\text{Cu} = \text{Cu}^{++} + 2\text{e}^-$ or its reverse). If it were referred to one "mole" of the kinetic unit reaction, the use of the stoichiometric number in (5) would have been avoided, just as this has been done in (4). If hydrogen scale (HS) values for the standard heat of reaction are applied, the values thereby obtained for the standard heat of activation are automatically also being referred to this arbitrary scale. So far, therefore, only relative values can be determined for the standard heat of activation of single electrode reactions, whereas absolute values can be determined for the mean standard heat of activation of mutually reverse reactions. In the present paper, this will be notified by writing (HS) in connection with relative values which refer to the hydrogen scale (*e.g.* $\Delta H_{\text{o,a}}^* = 2 \text{ kcal (HS)}$, $\Delta H_{\text{o,c}}^* = 44 \text{ kcal (HS)}$, and $\Delta H_{\text{o}}^*(\text{mean}) = 23 \text{ kcal}$, which are the values previously found for the $\text{Fe}/\text{Fe}_{\text{aq}}^{++}$ electrode reactions⁷). It is easily seen from (5) that the absolute values of the heat of activation of single electrode reactions are related to the corresponding hydrogen scale values by:

$$\Delta H_{\text{o,a}}^*(\text{absolute}) = \Delta H_{\text{o,a}}^*(\text{HS}) + (n/4\nu)\Delta H_{\text{o,a}}(\text{H}^+/\text{H}_2) \quad (6a)$$

$$\Delta H_{\text{o,c}}^*(\text{absolute}) = \Delta H_{\text{o,c}}^*(\text{HS}) + (n/4\nu)\Delta H_{\text{o,c}}(\text{H}^+/\text{H}_2) \quad (6b)$$

where n is the number of electrons in the thermodynamic reaction for the electrode reaction in question, ν is the stoichiometric number of this reaction (*not* the hydrogen electrode reaction), and the $\Delta H_{\text{o}}(\text{H}^+/\text{H}_2)$ terms are the absolute values of the standard heats of reaction of the hydrogen electrode.

This approach to the heat of activation of symmetric electrode reactions may easily be generalized to apply also to unsymmetric reactions (see Appendix).

3.0 EXPERIMENTAL

The materials and the method used in the present work, have been the same as described in the previous paper by the author¹ on the kinetics of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode at 20 and 25°C.

The present experiments have been carried out at approximately 0°C in an ice/water bath and at 15, 35, and 45°C in a water thermostat controlled to $\pm 0.1^\circ\text{C}$.

In all the experiments, the test electrolyte has been a hydrogen saturated 0.1 N sulphuric acid solution (made up at 20°C), and the potential measurements have been made against a saturated quinhydrone electrode in the same solution and of the same temperature as in the test cell.

The normal hydrogen scale (NHS) values of the reference electrode at the various temperatures were determined by measurements against a saturated quinhydrone electrode in 0.09 M potassium chloride + 0.01 M hydrochloric acid at the same temperatures. A saturated potassium chloride bridge was used in these measurements. The latter quinhydrone electrode has been ascribed the NHS-values:

0.605 V at 0°C
0.589 V at 15°C
0.566 V at 35°C
0.555 V at 45°C

These values have been estimated from the formula ²:

$$V = 0.7181 - 0.00071t(^{\circ}\text{C}) - (2.303 RT/F) \text{pH}$$

for the potential of the quinhydrone electrode as a function of temperature and pH, and from known values of the pH of the solution in question at various temperatures ².

4.0 RESULTS

The anodic potential-time curves obtained in the present work, are very much of the same type as those previously shown ¹ for analogous experiments at 20°C. The lowest potentials shown by these curves (these potentials mostly being the stationary potentials reached after some time of electrolysis) have been plotted in the Tafel diagram in Fig. 1.

The Tafel lines shown in Fig. 1, have all been drawn with a slope of

$$b_a = 2.303 RT/2F \quad (7)$$

which is in accordance with the previous results ¹ at 20 and 25°C. The reasonable fit of the experimental points to these lines do therefore strongly support the previous conclusion of the anodic Tafel slope being given by eqn. (7).

The Tafel lines in Fig. 1 have moreover been placed so as to make the average experimental deviation from these lines a minimum. By an extrapolation of these lines to the standard potential of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode (see the introduction to this paper), which according to deBethune *et al.*³ is given by:

$$E_o = 0.337 + 8 \times 10^{-6} (t - 25) V$$

where t is the temperature in °C, the following values are obtained for the standard exchange current (J_o) of this electrode in 0.1 N sulphuric acid solutions:

$$\begin{aligned} J_o &= (2.3 \pm 0.6) 10^{-3} \text{ A/cm}^2 \text{ at } 0^{\circ}\text{C} \\ J_o &= (1.2 \pm 0.3) 10^{-2} \text{ A/cm}^2 \text{ at } 15^{\circ}\text{C} \\ J_o &= (5.4 \pm 1.4) 10^{-2} \text{ A/cm}^2 \text{ at } 35^{\circ}\text{C} \\ J_o &= (1.4 \pm 0.3) 10^{-1} \text{ A/cm}^2 \text{ at } 45^{\circ}\text{C} \end{aligned} \quad (8)$$

The average deviations given, have been calculated from the average deviations of the experimental points in Fig. 1 from the Tafel lines. This implies the assumption that the Tafel slopes accepted (eqn. 7) are correct.

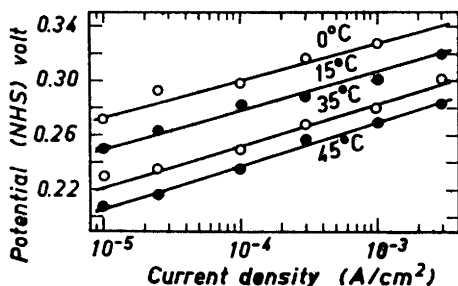
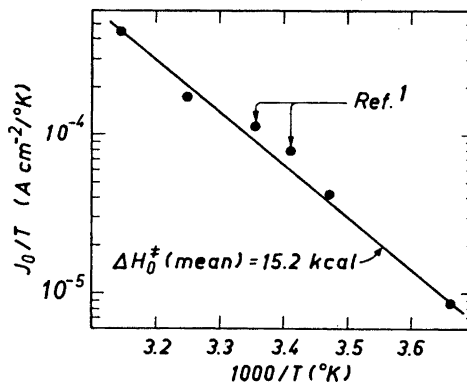


Fig. 1. Tafel diagram for anodic dissolution of copper in 0.1 N sulphuric acid at various temperatures.

Fig. 2. Arrhenius plot for the standard exchange current (J_0) of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode.



The average values in (8) give the following equations for the temperature dependence of the standard exchange current:

$$-R \, d(\ln J_0)/d(1/T) = 15.8 \pm 1.5 \text{ kcal} \quad (9)$$

$$-R \, d(\ln J_0/T)/d(1/T) = 15.2 \pm 1.4 \text{ kcal} \quad (10)$$

The latter relationship is graphically illustrated by the Arrhenius plot in Fig. 2, where also previously data by the author¹ at 20 and 25°C have been included.

The accepted value for the standard heat of reaction of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode is¹⁰:

$$\Delta H_{0,a} = -\Delta H_{0,c} = 15.4 \text{ kcal (HS)} \quad (11)$$

As further this electrode has been found¹ to be symmetric and to have a stoichiometric number of 1/2, the data in (10) and (11), on the basis of (2) and (5), give:

$$\Delta H_0^* \text{ (mean)} = 15.2 \text{ kcal} \quad (12)$$

and the following hydrogen scale values:

$$\Delta H_{0,a}^* = 30.6 \text{ kcal] (HS)} \quad (13a)$$

$$\Delta H_{0,c}^* = -0.2 \text{ kcal (HS)} \quad (13b)$$

for its standard heats of activation. The absolute values for the standard heat of activation of the two single electrode reactions should then be found by combining (13a) and (13b) with (6a) and (6b), when only the standard heat of reaction of the hydrogen electrode were reliably known.

The average values in (8) and (10) give the following Arrhenius equation for the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode:

$$\log (J_0/T) = \log (nF/\nu) + (1.54 \pm 0.05) - 15200/2.303 \, RT \quad (14)$$

showing the Arrhenius factor (A) to be given by:

$$\log (A/T) = 1.54 \pm 0.05 \quad (15)$$

where A is expressed in mole (activated complex)/cm² sec.

If the kinetics of the copper electrode reactions in this case is adequately covered by (1) and not dependent on factors representing the activity of surface sites, the present Arrhenius factor should, according to the transition state theory and the reasoning⁷ leading to (2), be given by:

$$\log (A/T) = \log (k/h) + \Delta S_o^*(\text{mean})/R \quad (16)$$

provided the transmission coefficient is equal to one. The mean standard entropy of activation, $\Delta S_o^*(\text{mean})$, which is defined analogous to (3), comes then out with a value of approximately $-40 \text{ cal/}^\circ\text{K}$.

5.0 DISCUSSION

From the present work on copper and previous work on iron⁷, we have the following standard heat data:

Electrode	:	Cu/Cu _{aq} ⁺⁺	Fe/Fe _{aq} ⁺⁺
$\Delta H_o^*(\text{mean})$:	15.2 kcal	23 kcal
$\Delta H_{o,a}^*$:	30.6 kcal(HS)	2 kcal(HS)
$\Delta H_{o,c}^*$:	-0.2 kcal(HS)	44 kcal(HS)
$\Delta H_{o,a} = -\Delta H_{o,c}$:	15.4 kcal(HS)	-21 kcal(HS)

The values for the heat of reaction have been taken from the compilation by Latimer¹⁰ and refer to the reaction of one gramatom of the metal. The heats of activation refer to the formation of one mole of the "activated complex".

A most striking feature of these results is that, for both the copper and the iron electrode, the mean standard heat of activation and the standard heat of reaction have very nearly the same numerical value, even though the values of the former are absolute ones (see Chapter 2.0) whereas those of the latter are hydrogen scale values. Through eqn. (5), this approximate equality further makes the hydrogen scale value of the standard heat of activation in one direction near to naught and in the reverse direction near to twice the numerical hydrogen scale value of the standard heat of reaction (as shown in the above table). This could possibly mean:

a) that the reactions of these metal/metal ion electrodes do not pass through any state of much higher enthalpy than that of the highest end state (initial or final), and

b) that the standard heat of reaction of the hydrogen electrode on the metals concerned is near to zero.

In connection with a), one has to remember that the end states according to the kinetic unit equation encompass *two* gramatoms (or gramions) of the metal.

What is said under a) is just what is well known to be the case for reactions between a crystal and its vapour. It seems thus likely that the exchange be-

tween a metal and aqueous solutions of its ions in this respect is analogous to the exchange between a crystal and its vapour, and that in the former field we should have much to gain from a wider application of the important developments which have occurred in the latter field during the last decade. As an example can here be mentioned that the double metal ion mechanism, which now has been found to govern both the iron and the copper electrode reactions, is analogous to the parabolic growth predicted by Burton, Cabrera, and Frank¹¹ for cases in which the mean displacement of adsorbed molecules on the crystal surface is small compared to the circumference of the critical two-dimensional nucleus. This will be more thoroughly discussed in a subsequent paper.

What is said under b) is not unlikely. This may be seen from the following scheme:

Reaction	ΔH_o (kcal)
$\frac{1}{2} \text{H}_2(\text{g}) = \text{H}^+(\text{g}) + \text{e}^-(\text{g})$	367.1
$\text{H}^+(\text{g}) = \text{H}^+(\text{aq})$	-256.0
$\text{e}^-(\text{g}) = \text{e}^-(\text{M})$	(-111.1)
$\frac{1}{2} \text{H}_2(\text{g}) = \text{H}^+(\text{aq}) + \text{e}^-(\text{M})$	(0)

The symbols (g), (aq), and (M) refer the species to the gas phase, the aqueous phase, and the metal phase, respectively. The ionization and hydration enthalpy values have been adopted from Latimer¹⁰ (p.35). The value of the electron transfer enthalpy corresponds to an electron work function of 4.85 eV, which is not far from many such data on copper and iron (according to the compilation by Michaelson¹²).

The present results on copper and previous results on iron⁷ give the following apparent values of the mean standard entropy of activation:

Electrode:	Cu/Cu _{aq} ⁺⁺	Fe/Fe _{aq} ⁺⁺
ΔS_o^* (mean):	-40 cal/°K	+12 cal/°K

We call these values apparent because of the underlying assumptions i) that the rate constants from which they have been determined, are adequately given by the usual product of a frequency factor (kT/h) and an entropy factor ($\exp(\Delta S_o^*/R)$) without including any catalyst activity (*e.g.* the activity of special surface sites), and ii) that the transmission coefficient is equal to one.

The former assumption represents a matter of great importance for our understanding of heterogeneous reactions in general and of electrode reactions in particular. This matter seems little clarified, and the validity of the assumption may be questionable. It is nevertheless of interest to work out the apparent standard entropy of the activated state of the copper and iron electrode and to compare this with the standard entropy of their end states. This may be

done by using the absolute metal entropy values tabulated by Latimer¹⁰ and the absolute ionic entropy values tabulated by Conway and Bockris¹³. The latter values are based on the standard entropy of electrons in metals being taken equal to zero, whereby we may ignore the electrons in the present treatment. On this basis, one arrives at the following standard entropy values at 15°C (cal/°K):

State	2Cu	(*)	2Cu ⁺⁺	2Fe + OH ⁻	(*)	2Fe ⁺⁺ + OH ⁻
S_o	+16.0	-68.5	-73.0	+15.5	-14.9	-69.3

The values given for the activated states have been calculated from:

$$\Delta S_o^*(\text{mean}) = \frac{1}{2}(\Delta S_{o,a}^* + \Delta S_{o,c}^*)$$

by the use of the end state entropies and the experimental values of the mean standard entropy of activation.

For the Cu/Cu_{aq}⁺⁺ electrode, the entropy data strongly support the enthalpy data in showing the activated state of this electrode to be closely related to the *ionic* end state. For the Fe/Fe_{aq}⁺⁺ electrode, the entropy data and the enthalpy data do not support each other that strongly, but are nevertheless mutually in agreement in indicating the activated state of this electrode to be relatively closely related to the *metallic* end state.

If some catalyst activities should be included in the experimental mean standard entropy of activation, the true value of this and thereby of the standard entropy of the activated state should be found by adding to the above values a term of:

$$- 2.303 R \log a$$

where a represents the product of the possibly included catalyst activities raised to the powers given by the stoichiometry of the catalyst interaction.

So far, it is difficult to say what a possibly might mean in the cases discussed here. However, it could have values down to about 10⁻⁸ for copper and about 10⁻⁷ for iron without the above mentioned correlation between the entropy and the enthalpy values being cancelled. It is also possible that such a correlation is not to be expected, whereby a may be even smaller. It could be of interest to compare this with step-lines in a crystal surface and kink sites on such step-lines. If the number of dislocations per cm² is 10⁸, the number of atomic sites on the step-lines connecting them need not exceed 10⁻⁴ of all sites in the area. The relative number of kink sites must be smaller, but not necessarily very much smaller. It seems thus not impossible that the experimental activation entropy values obtained may include a catalyst activity term representing for instance i) the proportion of step sites or of kink sites in the surface or ii) the product of these proportions or iii) the square of the one or the other of them. This question will be more thoroughly dealt with elsewhere.

APPENDIX

From the general theory of activation controlled electrode reactions¹⁴, we have:

$$\ln(J_0/T) = \ln(nFk/\nu h) + \Delta S_0^*/R - \Delta H_0^*/RT \pm \alpha n F \Delta \theta_0 / \nu RT \quad (1')$$

when the transmission coefficient and the transition state activity coefficient are assumed equal to unity and all possible catalytic interactions are accounted for. In the last term, + and - apply to anodic and cathodic reactions, respectively.

For two mutually reverse reactions, the sum of the symmetry factors is equal to one ($\alpha_a + \alpha_c = 1$), and we have from (1'):

$$\ln(J_0/T) = \ln(nFk/\nu h) + \Delta S_0^*(\text{mean})/R - \Delta H_0^*(\text{mean})/RT \quad (2')$$

where:

$$\Delta H_0^*(\text{mean}) = \alpha_c \Delta H_{o,a}^* + \alpha_a \Delta H_{o,c}^* \quad (3')$$

$$\Delta S_0^*(\text{mean}) = \alpha_c \Delta S_{o,a}^* + \alpha_a \Delta S_{o,c}^* \quad (4')$$

These are more general equations which include those used above for the special case of $\alpha_a = \alpha_c = \frac{1}{2}$.

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