

Heats of Activation of the $\text{Zn}/\text{Zn}_{\text{aq}}^{2+}$ Electrode

TOR HURLEN

Central Institute for Industrial Research, Blindern, Oslo, Norway

From measurements on the effect of temperature (0–40°C) on the anodic polarization of zinc in 0.001 M hydrochloric acid + 2.999 M potassium chloride and from known data on the isothermal temperature coefficient of the standard potential of this metal, the standard exchange current of the $\text{Zn}/\text{Zn}_{\text{aq}}^{2+}$ electrode has been found to obey the following Arrhenius equation:

$$J_0 = 6.1 \times 10^{10} (nFT/\nu) \exp(-25\,400/RT) \text{ A/cm}^2$$

showing a mean standard heat of activation of 25.4 kcal.

By comparison with corresponding results for iron and copper and by analogy considerations, indications are found for the mean standard heat of activation of these electrodes being an absolute measure of their standard heat of reaction. This gives –11.0 kcal as the most probable standard heat value for hydrogen evolution on zinc. On this basis, the results further show the standard heat of activation to be zero for zinc dissolution and 50.8 kcal for zinc deposition.

The results otherwise support previous data in showing a Tafel slope of approximately $2.303 RT/2F$ for the stationary anodic dissolution of zinc, both when under diffusion control and when under activation control. In unstirred solution, activation control predominates at temperatures below about 10°C, while diffusion control takes over at higher temperatures.

The possibility of obtaining absolute electrode potentials by combining kinetic and thermodynamic data is somewhat discussed.

1.0 INTRODUCTION

In a previous work¹, the zinc electrode reactions in strong chloride solutions have been shown to be symmetric ($\alpha = 1/2$) and to be represented by the kinetic unit equation:



showing the reactions to be second order ($\nu = 1/2$) with respect to the metal and the metal ions, respectively, and to be independent of the pH (see Ref.²). The same work clearly shows that the absolute rate of the anodic dissolution reaction at given potentials is independent of the zinc ion activity, and that the standard exchange current of the zinc electrode, therefore, is adequately

given by the intercept of its activation controlled anodic polarization curve in initially zinc free solution with its standard potential.

In the present work, advantage is made of the above findings in determining the standard heats of activation of the zinc electrode from measurements on the effect of temperature (0–40°C) on its anodic polarization in 0.001 M hydrochloric acid + 2.999 M potassium chloride. The theoretical basis for these determinations is as previously described³. The particular choice of electrolyte solution is first of all due to it belonging to the series of 3 M chloride solutions with which much work already has been done, and which has proved most suitable for the purpose (see Refs.^{1,2}).

2.0 EXPERIMENTAL

The materials and the slow galvanostatic polarization method used in the present work, have been the same as described in the previous paper by the author¹ on the kinetics of the $\text{Zn}/\text{Zn}_{\text{aq}}^{2+}$ electrode at 20°C.

The present experiments have been carried out at approximately 0°C in an ice/water bath and at 10, 30, and 40°C in a water thermostat controlled to 0.1°C. No stirring has been applied in the cell.

The potential measurements have been made isothermally against saturated calomel electrodes, which have been ascribed the following normal hydrogen scale (NHS) values⁴:

0.258 V at 0°C, 0.252 V at 10°C,
0.245 V at 20°C, 0.239 V at 30°C, and
0.232 V at 40°C.

No attempts have been made to correct for the possibly negligible liquid junction potential between the test solution and the saturated potassium chloride solution.

The standard NHS-potential of the zinc electrode is taken to be^{4,5}:

–0.765 V at 0°C, –0.764 V at 10°C,
–0.763 V at 20°C, –0.762 V at 30°C, and
–0.761 V at 40°C,

and its standard heat of reaction to be –36.4 kcal (NHS) in anodic direction⁵.

3.0 RESULTS

The weight changes found for anodes in the present work, verify previous findings in showing that the anodic reaction of the zinc electrode goes to the divalent state. The anodic potential-time curves obtained, are very much of the same type as those previously shown¹ for analogous experiments at 20°C. The lowest potentials shown by these curves are presented in a Tafel diagram plot in Fig. 1.

The lines in Fig. 1 have all been drawn with Tafel slopes of

$$b = 2.303 RT/2F \quad (2)$$

which is in accordance with previous results¹. The reasonable fit of the experimental points to these lines lends further confidence to the correctness of this Tafel slope value.

In Fig. 2, the current density values (J'_o) obtained by extrapolating the various Tafel lines in Fig. 1 to the corresponding standard potential of zinc, are presented in the form of an Arrhenius plot, $\log(J'_o/T)$ versus $1/T$. In the same diagram is also given the value previously determined¹

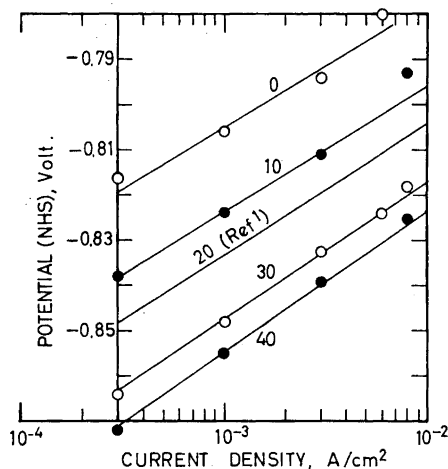


Fig. 1. Tafel diagram for anodic dissolution of zinc in unstirred solution of 0.001 M hydrochloric acid + 2.999 M potassium chloride at various temperatures (°C).

for the standard exchange current (J'_0) of the zinc electrode at 20°C. As suggested by the curves there drawn, J'_0 in the unstirred solution applied seems essentially identical to J_0 at temperatures up to about 10°C, but deviates more and more from it at higher temperatures. This indicates that the zinc electrode, at the lowest temperatures applied, is sluggish enough to make its anodic reaction essentially activation controlled even in unstirred solution, but that diffusion control to some extent comes in already at about 10°C and, from this

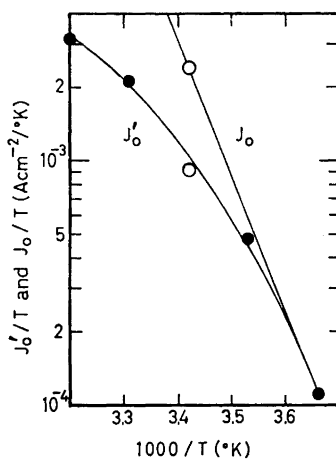


Fig. 2. Arrhenius diagram for the standard exchange current of the Zn/Zn_{aq}²⁺ electrode. The open circles represent results from Ref.¹

temperature on, increases in importance with increasing temperature until essentially pure diffusion control is attained. This change in control mechanism is obviously due to the ratio between the exchange current and the diffusion current at the zinc electrode increasing with temperature from a value small compared to 1 to a value appreciably higher than 1 within the temperature region covered by the present experiments (see eqn. (4) in Ref.¹). For zinc anodes in initially zinc free solutions, both the above currents may be regarded as being approximately proportional to the zinc ion concentration at the dissolving electrode surface, whereby the mentioned ratio becomes approximately independent of this concentration and essentially keeps its characteristic meaning also in the present case.

The straight line drawn for the standard exchange current (J_o) in Fig. 2, obeys the following Arrhenius equation:

$$J_o = 6.1 \times 10^{10} (nFT/\nu) \exp(-25\,400/RT) \text{ A/cm}^2 \quad (3)$$

where n is 2, ν is 1/2 (see the introduction to this paper), and the other factors have their usual meaning. This shows the mean standard heat of activation (as defined in Ref.³) to be:

$$\Delta H_o^*(\text{mean}) = 25.4 \text{ kcal} \quad (4)$$

which together with the symmetry factor of 1/2, the stoichiometric number of 1/2, and the accepted standard heat of reaction of the zinc electrode, $\Delta H_{o,a} = -36.4 \text{ kcal (NHS)}$, further gives (see eqn. (5) in Ref.³):

$$\Delta H_{o,a}^* = -11.0 \text{ kcal (NHS)} \quad (5a)$$

$$\Delta H_{o,c}^* = +61.8 \text{ kcal (NHS)} \quad (5b)$$

where the subscript (NHS) means that these energy values are referred to the normal hydrogen scale.

4.0 DISCUSSION

The present results support previous findings¹ in showing the anodic reaction of the zinc electrode in unstirred solution to be under mixed diffusion and activation control around room temperature. They further show that the former control mechanism gains predominance at higher and the latter at lower temperatures (below about 10°C), and verify that both of these control mechanisms give rise to a Tafel slope of $2.303 RT/2F$.

The mean standard heat of activation of 25.4 kcal(absolute) found for the zinc electrode in the present work, is distinctly lower than the numerical hydrogen scale value of 36.4 kcal for its standard heat of reaction. In this respect, the zinc electrode differs from the in many other respects similarly behaving divalent copper and iron electrodes, for both of which the above two standard heat terms are found to be very nearly numerically equal to each other³. This equality has been assumed to be an indication that the standard heat of reaction of the hydrogen electrode on iron and copper is near to zero³. The present results may thus analogously be taken as an indication of this *not* being true in the case of zinc as electrode material.

The previous results on iron and copper³ further indicate that the mean standard heat of activation of these metal/metalion electrodes is an absolute measure of their standard heat of reaction (the connection between heat of activation and heat of reaction thereby being quite analogous for metal/metalion electrode reactions as for reactions between a crystal and its vapour). Assuming this to be true also for zinc, one has the following two possibilities for the standard heat of reaction:

Reaction	Possibility I	Possibility II
Zn = Zn ²⁺ + 2e ⁻ (Zn)	+ 25.4 kcal	-25.4 kcal
2H ⁺ + 2e ⁻ (Zn) = H ₂	-61.8 kcal	-11.0 kcal
Zn + 2H ⁺ = Zn ²⁺ + H ₂	-36.4 kcal	-36.4 kcal

and, thereby, the following corresponding absolute values for the standard heat of activation of the mutually reverse reactions of the zinc electrode:

Reaction	Possibility I	Possibility II
Dissolution	50.8 kcal	0
Deposition	0	50.8 kcal

The values in the latter table are easily obtained by combining those in the former with (4) or (5) above (on the basis of (5) or (6) in Ref.³).

By a thermodynamic cycle as the one used in Ref.³ for the hydrogen evolution reaction, it is found that possibility I and II imply values of about 3.5 and 4.6 eV, respectively, for the heat of electron "evaporation" from zinc. For the electron work function of zinc, experimental values ranging from 3.08 to 4.65 eV are tabulated by Michaelson⁶. The highest of these are the most recently determined ones and probably also the most accurate ones. Unless zinc should have a surface potential of very large magnitude (one volt or so), this indicates that possibility II above is the most likely one.

If the mentioned indications on which the above treatment for zinc and the analogous treatment for copper³ and iron⁷ are based, should prove to be correct, an avenue is obviously open to the evaluation of absolute electrode potentials. These treatments give, namely, the heat of reaction of the single electrode reactions involved, and the entropy change accompanying these reactions is already known⁴. A calculation for iron, copper, and zinc thus yields the following values for the potential difference between metal and solution ($\Delta\phi = \phi_m - \phi_s$) at V(NHS) = 0 and 25°C (in Volt):

Fe	Cu	Zn
+ 0.216	+ 0.255	+ 0.498

These are then the values to be added to hydrogen scale values on these metals (at 25°C) to obtain absolute electrode potentials. However, the validity of the cardinal assumption on which these evaluations are based, namely

that the standard heat content of the activated state of the metal/metalion electrodes concerned is equal to that of their highest end state, remains to be proved. So far, only indications are obtained in this respect (see above and especially Ref.³). It may perhaps have some further support however, by the suggested relationship between heat of activation and heat of reaction in case not being a unique one for metal/metalion electrodes. Metal/metal-vapour reactions and also many atom exchange reactions in gases are well known to obey such a relationship. For the latter type of reactions, this relationship has recently even been derived theoretically⁸.

The Arrhenius equation (3) for the standard exchange current of the zinc electrode shows the Arrhenius factor (pre-exponential factor) to be:

$$A = 6.1 \times 10^{10}(nFT/\nu) \text{ A/cm}^2 \quad (6)$$

This may be compared to the corresponding values of 35 (nFT/ν) and $8.5 \times 10^{12}(nFT/\nu)$ previously found for the copper³ and the iron⁷ electrode, respectively, what shows this factor to vary strongly for metal/metalion electrodes. There seems to be no doubt that this variation mostly is due to differences in the mean standard entropy of activation of the various electrodes (as already discussed for iron and copper³). At present, however, our knowledge of possible other terms involved in the Arrhenius factor for metal/metalion electrodes is too incomplete for reliable values to be calculated for the activation entropy. Further calculations of the type previously performed³ for iron and copper in this respect, will therefore not be made here.

Acknowledgement. The author is much indebted to Miss Toril Tönderum and Miss Kari Storström for technical assistance, to various members of the staff at the Central Institute for Industrial Research for helpful discussions, and to the *U.S. Department of Army, European Research Office*, for financial support.

REFERENCES

1. Hurlen, T. *Acta Chem. Scand.* **16** (1962) 1337.
2. Hurlen, T. *Acta Chem. Scand.* **16** (1962) 1346.
3. Hurlen, T. *Acta Chem. Scand.* **15** (1961) 621.
4. deBethune, A. J., Licht, T. S. and Swendeman, N. *J. Electrochem. Soc.* **106** (1959) 616.
5. Latimer, W. M. *Oxidation Potentials (2nd Ed.)* Prentice-Hall, New York 1952, p. 168.
6. Michaelson, H. B. in *Handbook of Chemistry and Physics (38th Ed.)*, Chemical Rubber Publishing Co., Cleveland 1956–57, p. 2355.
7. Hurlen, T. *Acta Chem. Scand.* **14** (1960) 1564.
8. Kleinpaul, W. *Z. physik. Chem. (Frankfurt)* **29** (1961) 201.

Received December 22, 1961.