# TRUE TEMPERATURE COEFFICIENT OF THE ELECTRIC TENSION OF INDIVIDUAL ELECTRODES

## V. The Hg|HgO|OH⁻ electrode.[1] Preliminary investigation*)

By

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### Summary

The non isothermal temperature coefficient of the Hg|HgO|OH⁻ electrode is investigated and compared with the results of previous investigations. A comparison is also made between two different ways of evaluating the electric tension of the thermal liquid junction (e.t.t.l.j.) of the non isothermal whole cell. The difference between the mean values of $dU_0/dT$ obtained by applying both methods of evaluating the e.t.t.l.j. is rather small (about 13 $\mu$V/°C) and probably lies within the limit of experimental error. The values of $dU_0/dT$ calculated on the basis of the experimental data measured in this research are $-251.0$ and $-262.8$ $\mu$V/°C for the author's and the DE BETHUNE's approximation of evaluating the e.t.t.l.j. respectively. The first value is very close to the theoretical value calculated by DE BETHUNE.

## Introduction

Following the ideas[2] and the experimental techniques previously illustrated,[3] the electrode Hg|HgO|OH⁻ was considered as typical example of an electrode in strong alkaline medium, in order to obtain information on the behavior of this type of electrode, and to confirm that the elimination of the electric tension arising from the Soret effect at the initial state, made on the basis of the tabulated heats of transfer, is correct. This electric tension will be called in the following e.t.t.l.j.**)

In the meantime a paper by DE BETHUNE et al.[4] stresses once more the utility of a suitable salt bridge (saturated KCl) for correcting the temperature coefficients of the electrode electric tension for the e.t.t.l.j. This approximation by DE BETHUNE differs from that utilized in the previous papers of this

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  *) With the technical cooperation of Miss M. SOTTO.

 **) Electric tension of thermal liquid junction.

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series[5] in that it puts equal to zero the e.t.t.l.j. in a bridge of saturated KCl at 25°C under a temperature gradient $\left( i. e. \sum \frac{t_i Q_i}{z_i} = 0, \text{see below} \right)$, whilst the approximation utilized in this series puts the heat of transfer of the $Cl^-$ ion equal to zero (the DE BETHUNE approximation will be discussed in more detail in a future paper). The purpose of this preliminary note is limited to discussion of the value of the true temperature coefficient of the standard electric tension of the $Hg|HgO|OH^-$ electrode calculated on the basis of our experimental results and of some other values taken from the literature,[6,7] assuming both that $Q_{Cl^-} = 0$ at each concentration and that $\sum \frac{t_i Q_i}{z_i} = 0$ for a saturated KCl non isothermal bridge.

## Experimental

Only two papers may be found in the literature concerning this electrode, one by GOODRICH et al.[6] and another by IKEDA.[7]

The results obtained by these authors differ from those presented here by an amount which is significantly greater than the uncertainty due even to the relatively large experimental error of this particular electrode. A possible interpretation of this divergence is given below, but as matter of fact it may be stated that this electrode is very sensitive to various physical and chemical influences. Indeed this was one reason, for selecting this electrode for investigation. It is extremely sensitive to traces of $O_2$ and $CO_2$, to the physical nature and status of HgO (red crystalline, relatively roughly grained, obtained by the thermal reduction, or yellow very finely grained obtained by precipitation), to aging (attaining of the true thermodynamic equilibrium), etc.. Some operational differences are immediately detected in the technique utilized in the investigations cited and in that utilized in this research. GOODRICH[6] et al., for example, utilized yellow precipitated HgO, whilst red, thermally reduced, HgO is utilized in this investigation. On the other hand no particular mention is made by IKEDA[7] about the purification of the $N_2$ stream. The experiments performed during this investigation showed that consistent and reproducible results with this electrode can be obtained only when the following conditions are fulfilled:
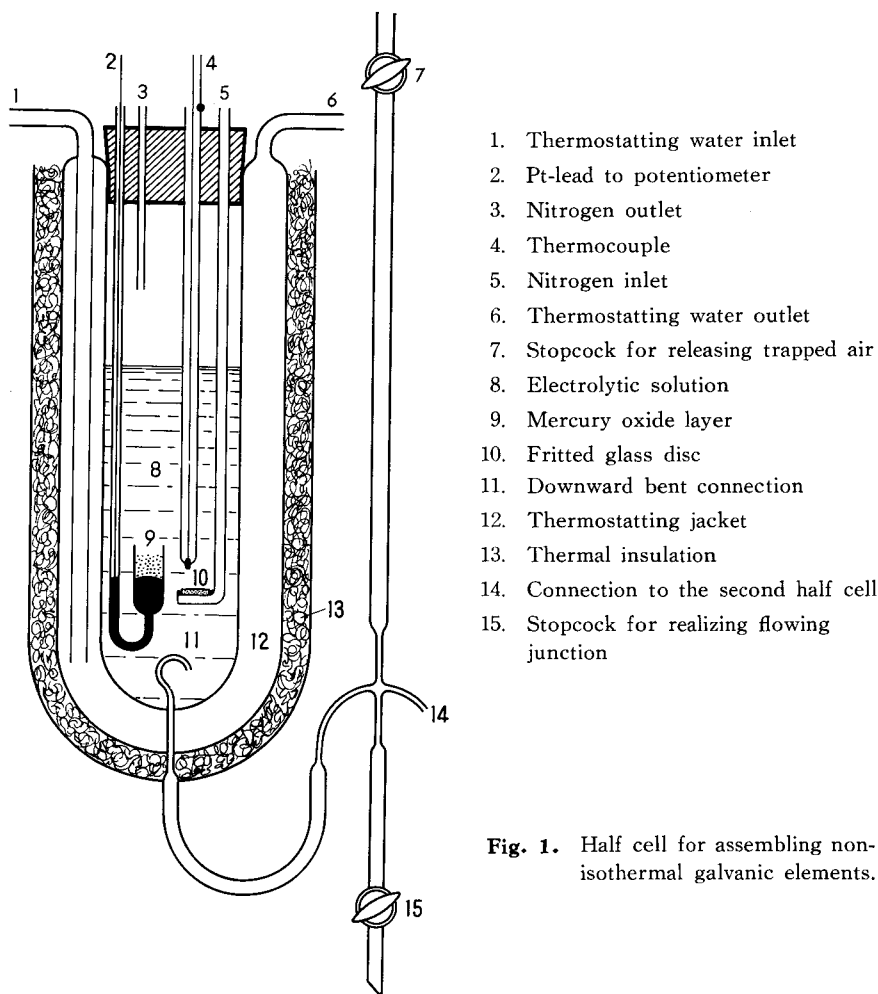
1. Most careful purification of all materials and of the $N_2$ stream bubbling through the electrode solution;

2. Sufficient time given for attainment of the equilibrium;

3. No HgO swimming in those portion of the solution outside the thermostatted cells (therefore at temperatures other than the nominal ones);

4. Use of red HgO obtained by very gentle thermal decomposition (of Hg (NO$_3$)$_2$) and thoroughly washed with distilled water and with the alkali solution under magnetic stirring. A glass covered stirring bar is to be preferred so that a gentle grinding action is also exercised for some equalizing of the graininess of HgO.

To fullfil condition n.3 a somewhat more sofisticated cell was constructed as shown in Fig. 1.

The cell was usually assembled and filled in the evening. The filling was made very slowly through the bottom tubing and the joining capillary bridge in order to avoid turbulence which would disturb the HgO deposited over Hg.



1. Thermostatting water inlet
2. Pt-lead to potentiometer
3. Nitrogen outlet
4. Thermocouple
5. Nitrogen inlet
6. Thermostatting water outlet
7. Stopcock for releasing trapped air
8. Electrolytic solution
9. Mercury oxide layer
10. Fritted glass disc
11. Downward bent connection
12. Thermostatting jacket
13. Thermal insulation
14. Connection to the second half cell
15. Stopcock for realizing flowing junction

**Fig. 1.** Half cell for assembling non-isothermal galvanic elements.

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It was then left overnight for attaining electrochemical and thermal equilibrium under a gentle $N_2$ flow through the solutions. The solutions in each half cell were separated during night by a gas bubble trapped within the joining capillary to avoid thermodiffusion. Preliminary testing showed that 12 hours are sufficient for attaining the thermal and electrochemical equilibrium. Measurement was started the following morning immediately after release of the air bubble in joining capillary bridge and after contact of the solutions. The measurements were considered reliable if they remained constant, within few units %, for at least an hour.

## Results and discussion

The results are collected in the Table 1. A short explanation illustrating the various steps needed to obtain the final value of $dU_0/dT$ is appropriate. The general equation utilized is:

$$\left(\frac{U}{\Delta T}\right)_{\text{meas. init.}} = \frac{dU_0}{dT} + \frac{R}{zF} \ln M + \frac{R}{zF} \ln f_{\pm}$$
$$+ \frac{RT}{zF} \frac{d \ln f_{\pm}}{dT} - \frac{1}{FT} \sum \frac{t_i Q_i}{z_i} , \qquad (1)$$

where $U$ is the experimentally measured electric tension on the non isothermal cell, $U_0$ is the standard electric tension at 25°C on the molality scale, $M$ is the molality of the solution, $f_{\pm}$ is the mean activity coefficient on the molal scale, $z$ is the valence of the electrochemically active ion (OH⁻), $t_i$ is the transference number, $z_i$ the valence and $Q_i$ the conventional heat of transfer of the ionic species $i$; the other symbols $R$, $T$ and $f_{\pm}$ have their usual meaning[*]. Considering that for this electrode $z = -1$, equation (2) is obtained after rearranging:

$$\frac{dU_0}{dT} = \left(\frac{U}{\Delta T}\right)_{\text{meas. init.}} + \frac{R}{F} \ln M + \frac{R}{F} \ln f_{\pm}$$
$$+ \frac{RT}{F} \frac{d \ln f_{\pm}}{dT} + \frac{1}{FT} \sum \frac{t_i Q_i}{z_i} \qquad (2)$$

The required numerical values for calculating the individual terms of equation (2) were taken from the literature.[8~10] The values in approximations I (columns 5 and 8 of Table 1) were obtained by putting $Q(Cl^-) = 0$ at every

[*] The *mean* activity coefficient was utilized in equations (1) and (2) instead of individual activity coefficient of the electrochemically active species OH⁻, because numerical values of the first one only are given in the tables of numerical values of physico-chemical quantities.

concentration and considering the conventional ionic heats of transfer given in the literature[10] as absolute heats of transfer. This approximation is supported by the statement that the global heat of transfer of LiCl is very small, nearly equal to zero, and by the statement that the values of $U/\varDelta T$ observed by GOODRICH *et al.*[6] for this non isothermal cell with LiOH, $(n\text{-}C_5H_{11})_4NOH$ and $(n\text{-}C_7H_{15})_4NOH$ as electrolyte are practically the same for the same molality. Owing to the fact that theoretically the heat of transfer of large symmetrical ions should be small and should approach zero with increasing size of the ions, it follows that the ionic heat of transfer of $Li^+$ should also be very small, thus justifying the approximation $Q(Cl^-)=0$.

The values in approximation II (columns 6 and 9 of Table 1) were obtained following de BETHUNE[11] by putting equal zero the e.t.t.l.j., *i. e.* the last term of equation (2) in the case that the temperature gradient is localized in a highly concentrated KCl solution (saturated at 25°C). Owing to the fact

TABLE 1. Non isothermal temperature coefficient of the
Hg |HgO| OH⁻ electrode, all values $\mu V/°C$.

| Electro-lyte | $M$ | $\dfrac{U_{\text{exp.}}}{\varDelta T}$ | $U/\varDelta T^{*)}$ $M, f_\pm, \dfrac{d\ln f_\pm}{dT}$ | $\dfrac{1}{FT}\Sigma(t_i Q_i/z_i)$ | | $corr^a$ KCl | $dU_0/dT$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | I | II | | I | II |
| LiOH | 0.01 | 707.1[b] | 305.7 | −486.8 | −521.7 | 11 | −181.1 | −205.0 |
| | 0.05 | 561.8[c] | 295.6 | −468.5 | −491.2 | 14 | −172.9 | −181.6 |
| NaOH | 0.01 | 661.0[b] | 260.1 | −442.8 | −477.7 | 11 | −182.7 | −206.6 |
| | 0.05 | 520.3[c] | 248.0 | −430.8 | −453.5 | 14 | −182.8 | −191.5 |
| | 0.10 | 467.6[c] | 249.3 | −431.8 | −450.0 | 17 | −182.7 | −183.7 |
| KOH | 0.01 | 617.0[b] | 215.2 | −401.7 | −436.4 | 11 | −186.5 | −210.2 |
| | 0.05 | 497.9[c] | 232.0 | −399.2 | −421.8 | 14 | −167.2 | −175.8 |
| | 0.10 | 403.0[c] | 200.4 | −401.5 | −419.8 | 17 | −201.1 | −202.4 |
| KOH | 0.014 | 516 [d] | 145.6 | −399.7 | −433.9 | 12 | −254.1 | −276.3 |
| | 0.014 | 537 [d] | 166.6 | −399.7 | −433.9 | 12 | −233.1 | −255.3 |
| | 0.100 | 332 [d] | 129.4 | −401.5 | −419.8 | 17 | −272.1 | −273.4 |
| | 0.100 | 359 [d] | 156.6 | −401.5 | −419.8 | 17 | −244.8 | −246.1 |

*) The values of $U/\varDelta T$ given in this column are corrected for the molality $(M)$, the activity coefficient $(f_\pm)$ and its temperature dependence $(d\ln f_\pm/dT)$.
a) Correction for KCl bridge, see text.
b) Values by GOODRICH *et al.* ref. 6.
c) Values by IKEDA ref. 7.
d) This research.

that in this case $z_+ = +1$, $z_- = -1$, $t_+ \simeq t_- \simeq 0.5$, it follows that $Q(Cl^-) \simeq Q(K^+)$ $\simeq 1/2\ Q(KCl)$. The e.t.t.l.j. for any other electrolyte can then be evaluated by considering the tabulated conventional ionic $Q$-values[10] decreased by $1/2$ $Q(K^+)$ for cations and augmented by same amount for the anions (thus maintaining constant the global value of the heat of the transfer for the whole electrolyte being considered at the concentration investigated). The value thus obtained of the e.t.t.l.j. must be finally corrected for the difference existing between saturated KCl and KCl of the concentration equal to that of the electrolyte being considered.*[)]

The values of $dU_0/dT$ for the Hg|HgO|OH$^-$ electrode following both criteria of evaluating the e.t.t.l.j. are given in the columns 8 and 9 of Table 1.

Some considerations are suggested by a careful inspection of these values.

1. It may be stated that the reproducibility of the final $dU_0/dT$ values is rather poor. This may be accounted for by the great sensitivity of this electrode to the presence of various impurities and to small differences concerning the actual physical and chemical working conditions. This electrode may be considered, in a certain sense, as a limiting case of bad reproducibility. Other electrodes investigated by the same technique, as for example, the Ag|AgCl|Cl$^-$ electrode, show in fact a much better reproducibility[5].

2. The scattering of the values obtained from the experimental data, even from the same author, is rather large. Nevertheless it may be stated that the correction arising from the last term of equation (2) is not at all negligible. In the case of the Hg|HgO|OH$^-$ electrode even the sign is inverted in going from the experimental $U/\Delta T$ value to the $dU_0/dT$ value.

3. The difference between the $dU_0/dT$ values obtained by applying the two different criteria of evaluating the e.t.t.l.j. is small and often smaller than the experimental scattering, showing that this difference will probably lie within the limit of the experimental error. No choice about the superiority of one criterion over the other one is thus possible and further investigations, perhaps with less sensitive electrodes, are necessary to decide this point.

4. Finally, it may be stated that the $dU_0/dT$ values obtained from the experimental data of this research are consistently lower (more negative) than those obtained from the experimental data of other investigators. The reason is not quite clear, but the deviation is consistent with the hypothesis that the KOH concentration really present in the cells of the other investigators was lower than the nominal one, perhaps because insufficient purification of the deoxygenating gas stream from $CO_2$ traces. If this hypothesis is correct, the

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*) These small corrections were interpolated from the values given in DE BETHUNE's paper.[11]

divergence between the values obtained in this research and those obtained from the experimental data found in the literature would become less important. A point supporting this hypothesis is that the mean value of $dU_0/dT$ obtained in this work by appliying approxmation I, $-251.0\ \mu V/°C$ is very close to the theoretical value calculated by DE BETHUNE, LICHT and SWENDEMAN,[12] $-249\ \mu V/°C$, whereas the mean value obtained from the same experimental data by applying approximation II is $-262.8\ \mu V/°C$, somewhat lower than the theoretical. However, this difference, about $13\ \mu V/°C$ is not of enough significance to give preference to the first criterion of evaluating the e.t.t.l.j.

## Acknowledgement

*Note added proof*: In a very recent paper by SHAMS EL DIN, KAMEL and ABD EL WANAB (J. Electroanal. Chem. **15**, 21 (1967)) attention is drawn on the very high sensitivity of the $Hg|HgO|OH^-$ electrode against accidental impurities, thus confirming once more our statement about the relatively bad reproducibility of this electrode and the difficulties of working with it.

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