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TEMPERATURE AND HYSTERESIS ERRORS IN CALOMEL HALF-CELLS

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ABSTRACT

Saturated and undersaturated KCl-calomel half-cells were subjected to temperature changes between 22.5 and 31.3° C and the difference in electromotive force (emf) between them and saturated calomel half-cells at 25° C was measured. During an 8° C change, maximum differences of 0.5 to 0.9 mv were found between the measured emf values and the equilibrium emf values corresponding to the temperature of the KCl solutions. Potentials within 0.2 to 0.3 mv of the equilibrium value were obtained in 2 to 3 hours after an 8° C change. Calomel half-cells protected with dewar flasks against small fluctuations in room temperature were more stable in potential than the unprotected cells. The saturated half-cell had a $\Delta E/\Delta T$ of 0.25 mv/°C and the undersaturated half-cell, 3.8 *N*, gave the value 0.47 mv/°.C One half-cell, saturated at 25° C. without an excess of KCl crystals, was measured and its $\Delta E/\Delta T$ was found to be erratic.

CONTENTS

I. INTRODUCTION

Calomel reference half-cells are used extensively in both electrometric titrations and pH work. Their potentials and temperature coefficients have been studied previously by other workers [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14].[1] The purpose of this report is to emphasize the errors which may be introduced into pH measurements by temperature changes affecting the potential of calomel half-cells.

Temperature changes of the calomel half-cell produce two effects on its potential: (a) the proportional increase in potential per degree rise in temperature, between two steady states, through the usual working range, 15 to 40° C; and (b) the lag or hysteresis in potential from values calculated from the temperature coefficient or potential change per degree, as previously reported by the authors and others [2, 3, 4, 7, 9, 11, 15]. It is preferred in this article to use the term change in potential per degree, $\Delta E/\Delta T$, rather than the temperature coefficient,[2] as it is simpler for general use. While temperature coefficients have long been recognized, there has been noticed in

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[1] Figures in brackets refer to the bibliography at the end of this article.

[2] The relationship between the temperature coefficient and $\triangle E/\triangle T$ is given by the following:

$$a_o=\frac{\Delta E}{\Delta T}\times\frac{1}{E_o}$$

where a_o=temperature coefficient and E_o=potential of the half-cell at some reference temperature.

some cases, particularly by the users of pH equipment in plant and mill operation, entire disregard of temperature effects on the results of pH measurements performed under varying conditions.

These investigations are given here to show the errors which may be present in reported pH values when the measurements are made with calomel half-cells under various temperature conditions; to emphasize the need for maintaining the half-cells at constant temperature for several hours before measurements can be made to an accuracy of 0.01 pH unit; to indicate the approximate difference of the emf measured under changing temperature conditions from that under equilibrium conditions; and to investigate a simple method for reducing the temperature changes of the calomel half-cell by insulation.

II. EXPERIMENTAL RESULTS

The mercury used in the preparation of the half-cells employed in these experiments was electrolytically purified, washed with nitric acid, and distilled. The calomel, containing finely divided mercury, was an excellent electrolytic preparation; and the KCl was a good chemically pure grade. The half-cells illustrated in figure 1 were made up and designated by letters as follows: Half-cells *G*, *N*, and *X*,[3] which are referred to in the text as saturated half-cells, were prepared with a mercury layer, *L*, covering the platinum contact wire *M*, to a depth of 1 to 1.5 cm and having a surface area of approximately 4 cm^2, and a calomel layer *K*, of 1 to 2 mm depth, a layer of KCl crystals, *J*, of about 1.5 cm depth, and a water solution of KCl, *O*, saturated at 25.0° C. Preliminary saturation of the KCl solution with calomel would have no measurable effect on the results reported. These half-cells were installed in dewar flasks *I*. Half-cell *H*, which is referred to in the text as the 4.1 *N* half-cell, was prepared in the same way as the preceding ones with the exception that the layer of KCl crystals was omitted. Half-cells *B*, *E*, and *L*, which are referred to in the text as 3.8 *N* half-cells, were prepared in the same way as *H*, with the exception that a 3.8 *N* KCl solution, which is saturated at about 20° C, was substituted for the 4.1 *N* solution. Half-cell *B* was not jacketed with a dewar flask but was left exposed to the air. Each half-cell was provided with a thermometer, *D*, graduated in 0.2° C divisions, which was immersed in the KCl solution to within 2.5 cm of the calomel layer. Calibrations of the thermometers showed a maximum deviation of 0.06° C from the graduated scale, and the readings were estimated to the nearest 0.1° C. The experimental half-cells were exposed to various temperatures between 22.2 and 31.3° C in a small, independent air bath, *B*, installed in a large constant-temperature room, *A*, kept at 25° C. The air bath was capable of being held constant to ±0.2° C at any temperature used and its temperature could be changed at the rate of 4 to 5° C/hr. The reference half-cells, indicated in figure 1, were arranged in the constant-temperature room outside of the air bath. A manifold, *S*, into which a 1-mm-capillary glass tube, *U*, from each of the half-cells led, and which was filled with a 4.1 *N* KCl solution containing an excess of solid KCl, was located in the constant-temperature room between the reference half-cells and those in the air bath. Each capillary tube contained a stopcock, *T*, to isolate the half-cell and prevent diffusion

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[3] These letters are specific for the half-cells in the text and have no reference to the schematic drawing, figure 1.

between measurements. Reservoirs in the air bath and in the constant-temperature room supplied KCl solutions through the glass tubes, *E*, for fresh junctions. Copper wires, *Q*, led from the mercury contacts, *N*, of each half-cell to mercury cups, *P*, into which the potentiometer leads, *R*, dipped.

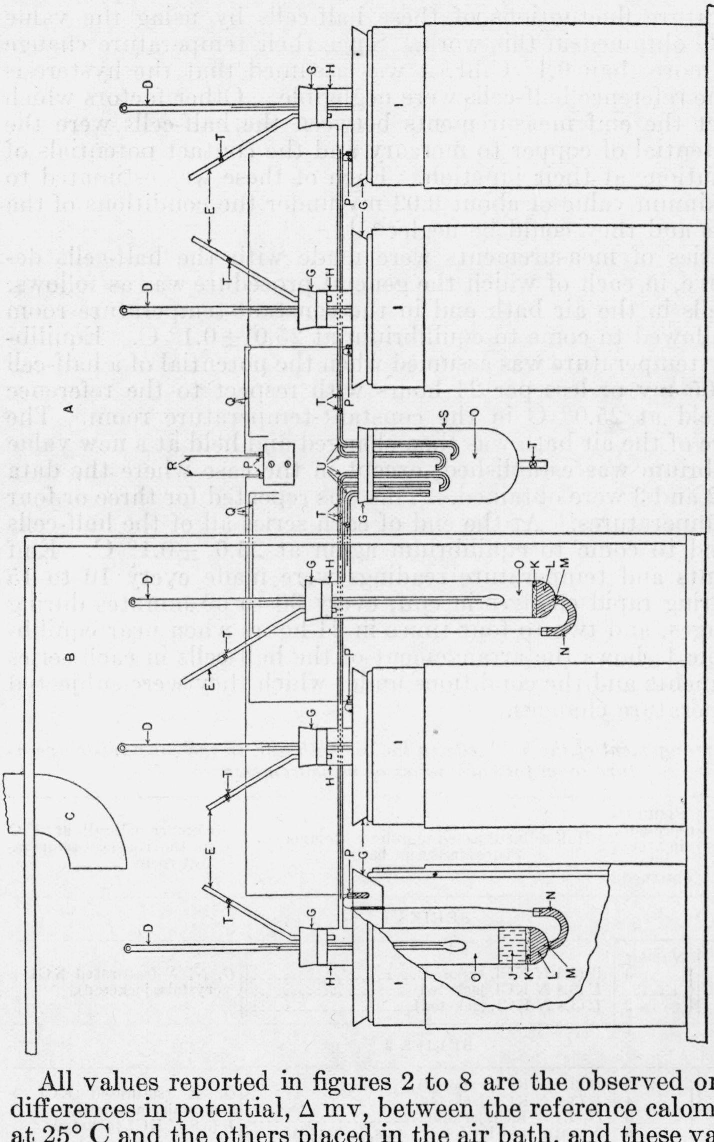

FIGURE 1.—*Details of the arrangement used in determining the effect of temperature on calomel half-cell potentials.*

A. Constant-temperature room.
B. Independent air bath.
C. Controlled air inlet.
D. Half-cell thermometers.
E. Leads to KCl reservoirs.
G. Rubber stoppers.
H. Half-cells.
I. Dewar flasks.
J. KCl crystals.
K. Calomel.
L. Half-cell mercury.
M. Sealed-in Pt wire.
N. Contact mercury.
O. KCl solution.
P. Mercury cups.
Q. Lead wires for half-cells.
R. Potentiometer leads.
S. Junction manifold.
T. Stopcocks.
U. Capillary salt bridges.

All values reported in figures 2 to 8 are the observed or calculated differences in potential, Δ mv, between the reference calomel half-cells at 25° C and the others placed in the air bath, and these values will be referred to throughout the text as the potential difference of the jacketed or exposed saturated system, 3.8 *N* system, etc. The emf was read to 0.001 mv with a Rubicon type *B* potentiometer and a reflecting type galvanometer with a sensitivity of 0.0005 μa/mm deflection at 1 m. The potentiometer readings were rounded off to the nearest 0.01 mv in the report. Although the room temperature was

25.0 ±0.1° C, the temperature of the reference half-cells varied from 24.7 to 25.2° C because of their proximity to the air bath and the radiation to and from it. As all of the observed potential differences, Δ mv, figures 2 to 8, of the half-cells subjected to temperature changes were expressed on the arbitrary basis that the average potential of the reference half-cells was zero at 25.0° C, corrections were applied for the temperature fluctuations of these half-cells by using the value 0.25 mv/° C obtained in this work. Since their temperature change was never more than 0.1° C/hr, it was assumed that the hysteresis effects in the reference half-cells were negligible. Other factors which might affect the emf measurements between the half-cells were the thermal potential of copper to mercury and the contact potentials of the salt solutions at their junction. Each of these was estimated to have a maximum value of about 0.02 mv under the conditions of the experiments and they could be neglected.

Three series of measurements were made with the half-cells described above, in each of which the general procedure was as follows: The half-cells in the air bath and in the constant-temperature room were first allowed to come to equilibrium at 25.0 ±0.1° C. Equilibrium at any temperature was assumed when the potential of a half-cell changed 0.05 mv or less per 24 hours with respect to the reference half-cells held at 25.0° C in the constant-temperature room. The temperature of the air bath was then changed and held at a new value until equilibrium was established, except in the case where the data for figures 2 and 3 were obtained. This was repeated for three or four different temperatures. At the end of each series all of the half-cells were allowed to come to equilibrium again at 25.0 ±0.1° C. Emf measurements and temperature readings were made every 10 to 15 minutes during rapid changes in emf, every 30 to 60 minutes during slower changes, and two to four times in 24 hours when near equilibrium. Table 1 shows the arrangement of the half-cells in each series of measurements and the conditions under which they were subjected to the temperature changes.

TABLE 1.—*Arrangement of the half-cells in the air bath and in the constant-temperature room for each series of measurements*

Maximum and minimum temperature of the air bath during each run	Figures representing the data obtained	Half-cells subjected to different temperatures in the air bath	Reference half-cells at 25° C in the constant-temperature room
		SERIES 1	
°C	*Number*		
24 to 31	3	B (3.8 *N* KCl, exposed)	*G, N, X* (saturated KCl + crystals, jacketed).
	--------	*E* (3.8 *N* KCl, jacketed)	
	2	*L* (3.8 *N* KCl, jacketed)	
		SERIES 2	
22.2 to 31.5	5	*B* (3.8 *N* KCl, exposed)	*G, X* (saturated KCl + crystals, jacketed). *L* (3.8 *N* KCl, jacketed).
	4	*E* (3.8 *N* KCl, jacketed)	
	8	*H* (4.1 *N* KCl, jacketed)	
	6	*N* (saturated KCl + crystals, jacketed)	
		SERIES 3	
25 to 31	--------	*B* (3.8 *N* KCl, exposed)	*G X,* (saturated KCl + crystals, jacketed). *L* (3.8 *N* KCl, jacketed).
	--------	*E* (3.8 *N* KCl, jacketed)	
	8	*H* (4.1 *N* KCl, exposed)	
	7	*N* (saturated KCl + crystals, exposed)	

The data obtained in the three series are represented graphically in figures 2 to 8. In each of these figures, the measured difference in potential, Δ mv, between a half-cell in the air bath and a reference half-cell at 25.0° C, are plotted against time in hours and represented by dots. For comparison, the temperatures of the KCl solution in the half-cell and of the air bath are plotted on the same scale. The ordinates of these curves were obtained by multiplying the average $\Delta E/\Delta T$ of the particular type of half-cell by the differences between the observed temperatures and 25.0° C. The half-cell temperatures are represented by circles and those of the air bath by crosses. In figures 2 to 8, the temperatures indicated refer to the air bath.

Figures 2 and 3 represent some of the data obtained from the first series of measurements, see table 1. These figures show the changes in the potential differences of the exposed and jacketed 3.8 *N* systems when the temperature of the air bath was decreased 1° C, held for 1 hr, and then returned to the original value.

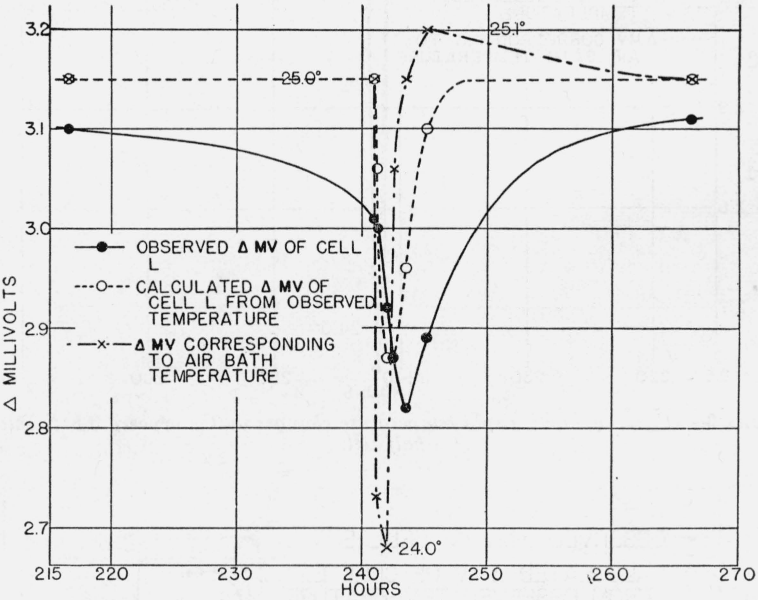

FIGURE 2.—*Effect of small, rapid temperature changes on the jacketed 3.8 N calomel half-cell.*

Figures 4, 5, 6, and part of 8 represent the data obtained in the second series of measurements. Figures 4[4] and 5 show the changes in the potential differences of the exposed and jacketed 3.8 *N* systems during increasing and decreasing temperatures.

Figures 7 and part of 8 represent some of the data obtained in the third series of measurements. Figures 6 and 7 show the changes in the potential differences of the exposed and jacketed saturated systems with solid KCl present, and figure 8 shows those of the 4.1 *N* system at temperatures above and below its saturation point.

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[4] Half-cell *E*, with values recorded in figure 4, was of different construction from the others. It was a 4-pocket, vertical cell, 4 half-cells in one container, with the mercury cups arranged in balconies one above the other and a common central opening extending the height of the cell and filled with the KCl solution. The Pt contact was near the surface of the Hg and the potentials of the individual half-cells varied when the container was handled. Half-cell L, similar in make-up to *E*, showed a temperature coefficient which was identical to that of the exposed type, but insufficient readings were made during the rise and fall of the temperature to determine the steep portion of the curve with any degree of accuracy.

In order to check the possibility that the temperature of the KCl solution and the mercury in a half-cell did not change at the same rate during an increase or decrease in the temperature of the air bath, a cell was arranged with two thermometers, one with its bulb completely

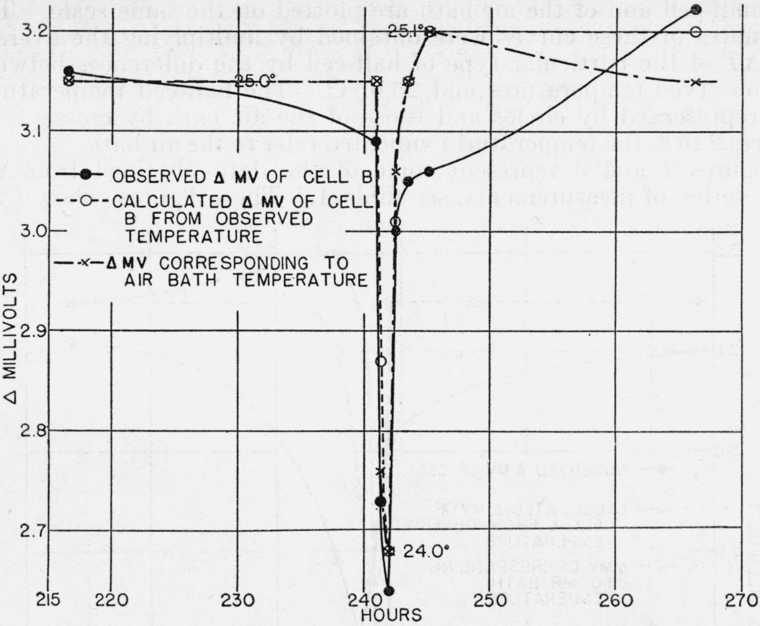

Figure 3.—*Effect of small, rapid temperature changes on the exposed 3.8 N calomel half-cell.*

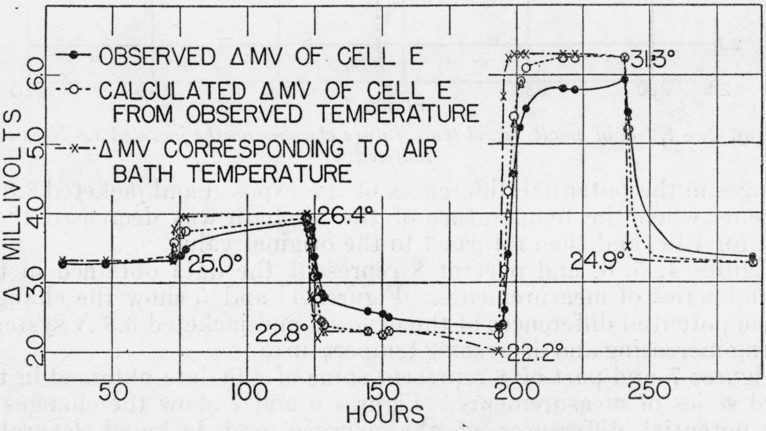

Figure 4.—*Effect of small and large temperature changes on the jacketed 3.8 N calomel half-cell.*

Approximate Hg temperatures are represented by triangles on the emf scale.

immersed in the mercury of the half-cell and the other extending to within 2.5 cm of the mercury and immersed in the KCl solution. The thermometer whose bulb was in the KCl solution corresponded to the position of those in the half-cells used in obtaining the data for figures 2 to 8. The half-cell was subjected to changes in temperature in both the exposed and the jacketed state, which were comparable to those represented in figures 4 to 8, and the two thermometers were read at various time intervals so that the temperature-time relationships of the two liquids and the air bath could be correlated. The data obtained showed that during changes of temperature in the air bath there was a difference in temperature between the KCl solution and the mercury. This difference began with the first change in the temperature of the half-cell and increased rather rapidly during the first half of the total temperature increase or decrease, and then gradually decreased as the temperature of the two liquids approached that of the air bath. Table 2 shows the maximum differences between the temperatures of the mercury and the KCl solution for the saturated

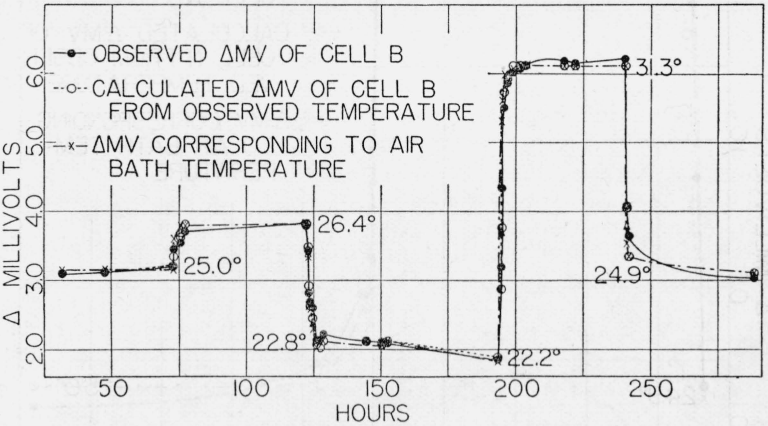

FIGURE 5.—*Effect of small and large temperature changes on the exposed 3.8 N calomel half-cell.*

Approximate Hg temperatures are represented by triangles on the emf scale.

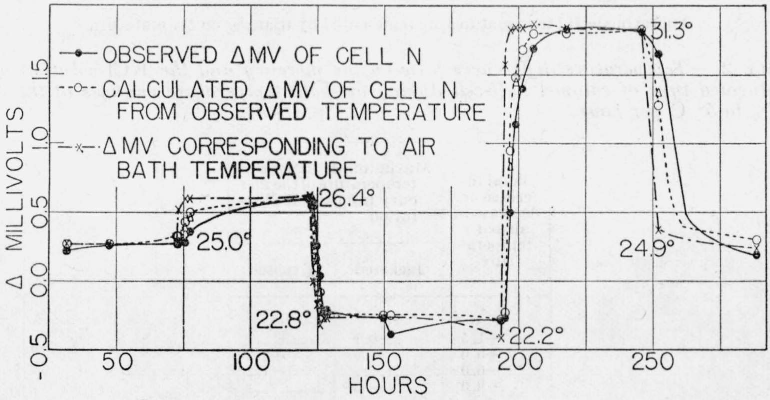

FIGURE 6.—*Effect of small and large temperature changes on the jacketed saturated calomel half-cell.*

Approximate Hg temperatures are represented by triangles on the emf scale.

type of half-cell. Similar effects were observed in the 3.8 *N* half-cell but with slight differences in magnitude. Some approximate points corresponding to the Hg temperatures are plotted in figures 4 to 7 and are indicated with triangles.

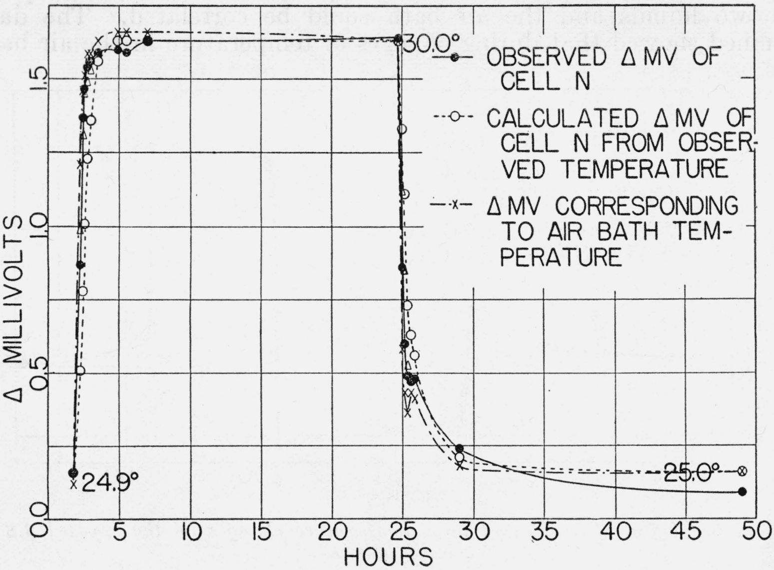

FIGURE 7.—*Effect of large temperature changes on the exposed saturated calomel half-cell.*

Approximate Hg temperatures are represented by triangles on the emf scale.

TABLE 2.—*Temperature differences between the mercury and the* KCl *solution of a saturated type of calomel half-cell during air-bath temperature changes at the rate of 4 to 5°* C *per hour*

Total increase or decrease in air-bath temperature	Maximum deviations in temperature of the mercury from the KCl solution	
	Jacketed	Exposed
°C	°C	°C
+1.5	−0.1	----------
+6.0	−.9	+2.2
−6.0	----------	−1.2
−8.0	+.3	----------

III. DISCUSSION

The dewar flasks surrounding the half-cells retarded the effect of changing external temperature on their temperatures and potentials. For small fluctuations in temperature, figures 2 and 3, the observed potential difference of the jacketed system was less and the potential difference of the exposed system was greater in amount than that calculated from the air bath temperature. Thus, for small changes above and below a uniform temperature, the potential difference of a jacketed system was subject to smaller changes than the exposed type. For small temperature changes in one direction, in the first portion of the curves in figures 4, 5, and 6, there was a period of several hours in which the potential difference of the jacketed system did not change appreciably, while that of the exposed system followed the temperature almost immediately.

When the temperature of the air bath was increased 8° C in 2 hours and maintained at the higher value, the following effects were observed, depending upon the type of half-cell and persisting for about 60 to 80 percent of the rise. The potential differences of the jacketed systems lagged behind the equilibrium potential difference corresponding to the temperature of the KCl solution by 0.5 to 0.9 mv, 0.3 to 0.8 mv behind that corresponding to the Hg temperature, and 2 to 3 mv behind that corresponding to the air bath temperature; see figures 4 [5] and 6. These differences then gradually became smaller

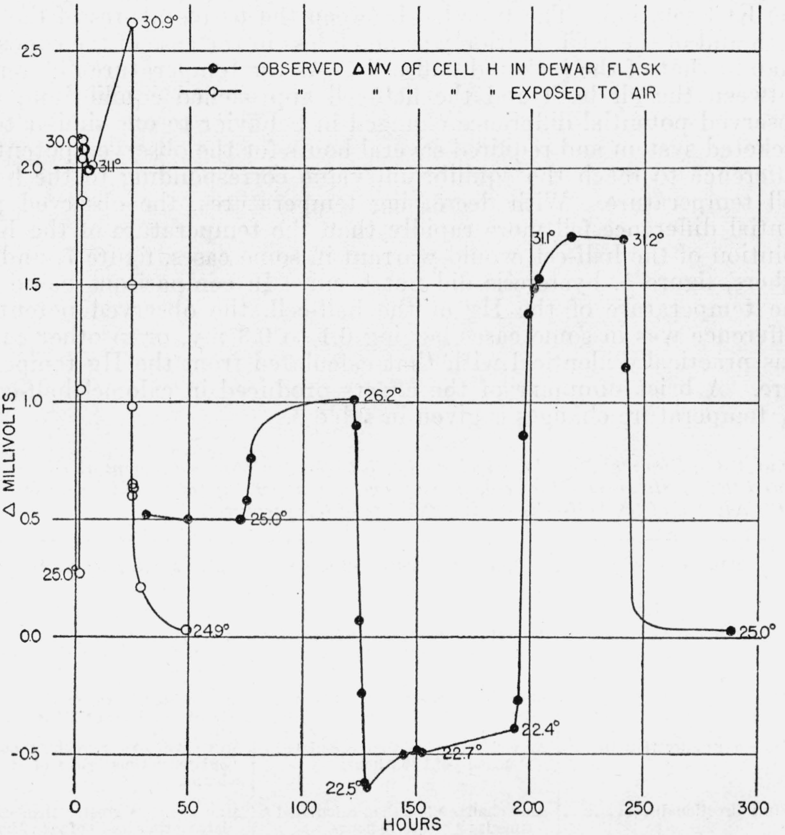

FIGURE 8.—*Effect of temperature changes above and below its saturation point on the potential of a 4.1 N calomel half-cell.*

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[5] The behavior of this half-cell cannot be analyzed too closely, see footnote 4, and only its general concordance can be assumed.

until equilibrium was established. With a falling temperature, the hysteresis again occurred, but to a less extent. After the air-bath temperature began to increase, 1 to 2 hours elapsed before an appreciable temperature increase was observed in the half-cell temperature. This time lag slowly increased to 5 to 7 hours near the new temperature level. On the other hand, in the exposed half-cells, figures 5 and 7, the observed potential differences of these systems increased more rapidly than the equilibrium values corresponding to the temperatures of the KCl solution, but the reverse occurred if the equilibrium values corresponding to the Hg temperatures were substituted for those of the KCl solution. The time lag between the temperatures of the air bath and of the KCl solution was much less in the case of the exposed than in that of the jacketed half-cells. As the temperature difference between the air bath and the half-cell approached equilibrium, the observed potential difference changed in behavior to one similar to a jacketed system and required several hours for the observed potential difference to reach the equilibrium value corresponding to the half-cell temperature. With decreasing temperatures, the observed potential difference fell more rapidly than the temperature of the KCl solution of the half-cell would warrant in some cases, figure 7, and in others, figure 5, hysteresis did not occur. In comparisons based on the temperature of the Hg of the half-cell, the observed potential difference was in some cases lagging 0.1 to 0.3 mv, or in other cases was practically identical with that calculated from the Hg temperature. A brief summary of the effects produced in calomel half-cells by temperature changes is given in table 3.

TABLE 3.—*Summary of the relationships between the observed potential differences and the equilibrium values calculated from the temperature of the* KCl *solution and the* $\Delta E/\Delta T$ *of the half-cells during changes of temperature*

Temperature change in bath	Effect on jacketed half-cells [a]	Effect on exposed half-cells [a]
°C		
±1 (rapid fluctuations)	Δmv change [b] less than calculated [c] time lag [d] several hours.	Δmv change [b] greater than calculated [c] time lead [e] of less than 1 hour.
+1.5 (unidirectional) [f]	Δmv change [b] less than calculated [c] time lag [d] of 6 to 7 hours.	Δmv change [b] greater than calculated [c] time lead [e] of 1 to 2 hours.
−3 to −6 (unidirectional) [f]	Δmv change [b] less than calculated [c] time lag [d] of 1 to 7 hours.	Δmv change [b] = or greater than calculated [c] time lead [e] of ½ to 2 hours.
+8 (unidirectional) [f]	Δmv change [b] less than calculated [c] time lag [d] of 2 to 10 hours.	Δmv change [b] greater than calculated [c] time lead [e] of ½ to 2 hours.

[a] The magnitude of the differences between the observed and calculated potentials for the exposed and jacketed systems of the same type were of the same order but opposite in effect.

[b] Observed potential difference.

[c] Calculated from the temperature of the KCl solution and the $\Delta E/\Delta T$ of the half-cells.

[d] Time required for the observed potential differences to equal the values calculated from the temperatures of the KCl solution.

[e] Time required for the values calculated from the KCl solution temperatures to equal the observed potential differences,

[f] Temperature change between two steady states.

In comparing the behavior of the three types of half-cells, it will be noticed that while the $\Delta E/\Delta T$ of those saturated at all temperatures used and those undersaturated, 3.8 N, are different in magnitude, they behave in a similar and rather consistent manner.[6] On the other

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[6] See footnotes 4 and 5.

hand, the half-cell saturated at 25.0° C and without an excess of solid KCl, showed an inconsistent $\Delta E/\Delta T$ as well as a variation of 0.4 to 0.5 mv in the equilibrium potential at 25.0° C. The variable $\Delta E/\Delta T$ was probably due to the half-cell acting first as a supersaturated half-cell and then as one saturated with an excess of crystals at temperatures below 25.0° C and as an undersaturated half-cell at temperatures above 25.0° C. In considering the potentials measured in the saturated system, it is possible that part of the value might be attributed to a concentration or diffusion potential of the KCl solution. It would then follow that the saturated system should show a long drift while reaching equilibrium or an overshoot in voltage. This did not occur to a more noticeable extent in the saturated system than in the 3.8 *N* system and it can safely be assumed that the concentration potential is negligible when considering the precision of the values reported.

The data obtained in the experiments were not precise enough to allow any satisfactory interpretation of the mechanism of the calomel half-cell during a changing temperature. The large temperature difference between the Hg and the KCl solution and the small thickness of the boundary region would make the accurate determination of the interface temperature extremely difficult, and would also introduce a temperature gradient effect on the potential of the half-cell. The temperature of the interface of the Hg–HgCl in the half-cell would be at some value between those observed for the Hg and the KCl solution. The equilibrium potential difference corresponding to the interface temperature would probably agree more closely with the observed potential difference than did the values corresponding to the Hg or the KCl solution.

The results showed, however, that stable conditions of temperature should exist for some time, 2 to 3 hours for the exposed half-cells and 7 to 10 hours for those in the dewar flasks, to establish equilibrium values that will be accurate to within 0.2 to 0.3 mv and satisfactory for precise pH work. Magoji [7] reported that 30 to 40 minutes was required for calomel half-cells to reach equilibrium after a 5° C temperature change. His work was performed in a water bath, where the rate at which a temperature equilibrium is established would be more rapid than in air. This would probably account in part for the difference in time found by him for the cells to reach equilibrium. In addition, the size of the half-cell would affect the rate at which equilibrium is attained.

In any case, calomel half-cells require much shorter time periods to reach equilibrium after a temperature change than they do to reach equilibrium when freshly prepared. This latter time period has been variously reported to be 2 days to 2 weeks [4, 7, 11]. The exposed half-cells would be more serviceable under conditions where large and rapid temperature changes, 3° C or more per hour, occur. For small fluctuations in temperature, the jacketed half-cell would be more serviceable, as the potential would be less variable and near a value corresponding to the mean temperature. There is apparently very little choice between the saturated and the undersaturated half-cells if only reproducibility and the time required to reach equilibrium at a new temperature are considered. However, the undersaturated half-cells have a larger $\Delta E/\Delta T$ than the saturated type and, furthermore, their potentials would have to be determined for the concentration of KCl solution used, unless standard buffers and a hydrogen electrode are used in the calibration of a cell system. This, together with the difficulty of preventing evaporation and an accompanying change in the value of the half-cell, would indicate that the saturated type with an excess of crystals would be more serviceable for general use.

The $\Delta E/\Delta T$ of the saturated half-cell with an excess of solid KCl was found to be 0.25 mv/° C, and that of the 3.8 *N* KCl half-cell to be 0.47 mv/° C. Ewing [5] gives the saturated half-cell a $\Delta E/\Delta T$ of 0.20 mv/° C, and Bjerrum and Unmack [2] the value 0.22 mv/° C. The value obtained in this work agrees fairly well with the above results considering that only one half-cell was used in its determination. Taking the value 0.2 mv/° C as the $\Delta E/\Delta T$ of the calomel half-cell and the value −0.76 mv/° C [3] for the cell,

$$-\mathrm{Pt},\ \mathrm{H_2}(1\ \mathrm{atm})\,|\,\mathrm{HCl}(1\ N)\,\|\,\mathrm{KCl(saturated)}\,|\,\mathrm{HgCl},\ \mathrm{Hg}+,$$

then the $\Delta E/\Delta T$ of the hydrogen half-cell together with the liquid junction must be in the neighborhood of +1.0 mv/° C. This would indicate that the temperature of the hydrogen half-cell is the most important factor in the variation of the cell combination: saturated calomel-Pt−H_2. It has been customary, however, to assume the $\Delta E/\Delta T$ of the hydrogen half-cell to be zero and to throw the entire weight of the emf change on the companion reference half-cell. Under varying conditions encountered in commercial laboratories, as in the measurement of the pH of a solution having a temperature different from that of the reference half-cell, considerable error may be introduced when one half-cell is calculated to a value corresponding to the temperature of the companion half-cell by the use of the over-all $\Delta E/\Delta T$ of the cell. It should again be emphasized that for more precise and reproducible results the temperature of the cell system and the unknown solution, if possible, should be constant for several hours before measurements are made.

IV. CONCLUSIONS

The jacketing or insulating of calomel half-cells with dewar flasks does not eliminate the hysteresis, but in the case where small, fluctuating temperature changes are encountered the magnitude of the variation in potential is reduced.

Errors due to hysteresis in a jacketed half-cell during a temperature increase may amount to 0.5 to 0.9 mv, which is equivalent to 0.01 to 0.02 pH, depending on the type of half-cell, and 0.4 to 0.5 mv for exposed half-cells, when the temperature change is 6 to 8° C at a rate of 4 to 5° C/hr, and the temperature of the half-cell is taken as that of its KCl solution. Under similar conditions a drop in temperature of 6° C may give a hysteresis error of 0.5 mv.

Temperature differences were found between the Hg and the KCl solution of a half-cell during changes in temperature of the air bath. These varied from 0.1 to 2.2° C, depending on the magnitude of the change, at a uniform rate, in the temperature of the air bath. In the exposed half-cells, the Hg temperature was higher than that of the KCl solution during an increase and lower during a decrease in temperature of the air bath. The reverse occurred in the jacketed half-cell.

In determining the temperature of a half-cell for voltage corrections, it should be measured inside the half-cell and as close to the Hg interface as possible, rather than in the surrounding air.

The half-cell with an excess of solid KCl and hence saturated near the Hg interface at all temperatures used, had a $\Delta E/\Delta T$ of 0.25 mv/° C over the range 22.5 to 31.3° C. The 3.8 N half-cell, undersaturated at all temperatures used, had a $\Delta E/\Delta T$ of 0.47 mv/° C for the above range. The half-cell saturated at 25° C showed a variable and inconsistent $\Delta E/\Delta T$.

Care should be taken in the control and measurement of the temperature of a hydrogen half-cell during pH measurements as the apparent $\Delta E/\Delta T$ of this half-cell together with the liquid junction potential is in the neighborhood of 1.0 mv/° C and large errors could be introduced.

In pH measurements requiring an accuracy of 0.1 pH, temperature variations of 4 to 5° C could be tolerated without temperature corrections. For precision results to 0.01 to 0.02 pH, the measurements should be made in constant temperature air or liquid baths and after the temperature of the cell system has been uniform for several hours.

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