[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY OF VANDERBILT UNIVERSITY]

STUDIES ON THE TEMPERATURE COEFFICIENTS OF REFERENCE ELECTRODES

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The interest which is now being shown in electromotive-force studies is closely related to the recently developed appreciation of the value of accurate knowledge of the free energy of chemical reactions, the activity of solutes, hydrogen-ion concentration and related phenomena, and this interest is in turn demanding more reliable information concerning a few commonly used reference electrodes. Clark[1] has given considerable space to a discussion of the present status of our knowledge of reference electrodes, especially those used in hydrogen-ion work, and has pointed out the advisability of clinging to certain arbitrary and perhaps less accurate values for these electrodes until certain theoretical points are settled and further experimental work is done. One of the points of uncertainty is the effect of temperature upon the potential of reference electrodes and it is to this subject that attention is given in this paper.

Two methods have been used in previous work to ascertain the temperature coefficients of electrodes. In the method most commonly used the effect of temperature upon a complete cell, one electrode of which is a hydrogen electrode, is studied experimentally and from these data and the assumed behavior of the hydrogen electrode, the temperature coefficient of the other electrode is calculated. This method leaves in doubt the influence of temperature upon the practical hydrogen electrode which constitutes part of the complete cell. The second method is that in which the two halves of the cell are kept in separate thermostats, the temperature of one electrode is kept constant and the change in the e.m.f. of the complete cell when the temperature of the second electrode is varied is considered a measure of the temperature coefficient of the second electrode.

The first method outlined above was used by Lewis and Randall[2] to determine the temperature coefficient of the 0.1 N potassium chloride-calomel electrode. Because of the extensive use of this electrode in hydrogen-ion work Clark[1] presents this determination as the best source of information concerning the effect of temperature on this electrode.[3] In this development Lewis and Randall state that the e.m.f. of the cell H_2, HCl (0.1 M)::H^+ (M), H_2; $E = 0.0684$ ($E = 0.0644$ according to

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[1] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., **1923**.

[2] Lewis and Randall, THIS JOURNAL, **36**, 1969 (1914).

[3] These writers refer all electrode potential values to that of the standard molal hydrogen electrode and consider the latter to have zero potential at all temperatures.

Lewis, Brighton and Sebastian)[4] may be assumed without serious error to be proportional to the absolute temperature. This assumption is probably based upon the Nernst relation and since the activity of the hydrogen ion in the standard hydrogen electrode is equal to unity at all temperatures by definition, this assumption would be correct only in the event that the activity of the hydrogen ion in the practical 0.1 M hydrogen electrode did not vary with temperature. The data of Fales and Mudge[5] and those herein presented indicate that in practical hydrogen electrodes the activity of the hydrogen ion increases with temperature. Doubt concerning the validity of the assumption made at this step in the development leaves the accepted value for the temperature coefficient of the calomel electrode also in doubt. The first method of determining temperature coefficients will give reliable results only after the effect of temperature on certain practical half-cells is determined—perhaps by the second method.

Fales and Mudge[5] in studying the saturated calomel electrode have used the second method outlined above to determine the temperature coefficient of this electrode. A cell of the type, $A:A^+B^-$ (n M, X°C.)::-A^+B^- (n M, Y°C.):HgB:Hg, is studied. One of the two electrodes is kept at a constant temperature while the temperature of the second is varied, and the change in the e.m.f. of the complete cell is considered a measure of the temperature coefficient of the second half. This method gives the temperature coefficient of an electrode with reference to a second practical electrode at a constant temperature, usually 25°. If the potential of the second electrode on the hydrogen scale is known, the potential of the first electrode is established at all temperatures with reference to the standard hydrogen electrode at 25°. Other writers[6] would express the potential of an electrode at each temperature with reference to the standard hydrogen electrode at the *same* temperature. These two methods of expressing potentials may be harmonized if the influence of temperature on the potential of the standard hydrogen electrode is established or if this electrode is considered to have a constant potential. Since other properties of the standard hydrogen electrode are also arbitrarily defined, the latter suggestion seems admissible.

Further analysis of the second method shows that there is a type of liquid junction, which may be designated a *liquid-temperature junction*, peculiar to this method of determining temperature coefficients. Cells may be used in these experiments as in other electrode potential studies which are free from the usual liquid junctions, but in the experiments of the second method an e.m.f. may be developed where the electrolyte of

[4] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

[5] Fales and Mudge, *ibid.*, **42**, 2434 (1920).

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 402.

one temperature meets a *similar* liquid of a different temperature. Any e.m.f. so developed is considered a part of the potential of the electrode under investigation. The first method will give electrode potential values which are free from the liquid-temperature complication when the potentials of the reference electrodes used in the experimental work have been established on the hydrogen scale for temperatures other than 25°.

Since the second method for determining the temperature coefficients of electrode potentials is free from assumptions and gives valuable information concerning these electrodes, this method seems worthy of pursuit and was used in the studies herein presented. The effect of temperature on the potential of two hydrogen electrodes containing sulfuric acid as the electrolyte and two mercurous sulfate electrodes has been determined.

Experimental Part

Two sets of cells of the type, (Pt) H_2, H_2SO_4 (*n N.*), Hg_2SO_4, Hg, were studied. One set consisted of hydrogen electrodes and mercurous sulfate electrodes having 0.1000 *N* sulfuric acid as the electrolyte and the other set was similar except that the electrolyte was 1.0004 *N* sulfuric acid. The hydrogen electrodes were kept in one thermostat and the mercurous sulfate electrodes in a second and the two halves were connected through a bridge of sulfuric acid of the same strength.

In each experiment at least four hydrogen electrodes and four mercurous sulfate electrodes were used and they were so bridged that any one of the four hydrogen electrodes could be measured against any one of the four mercurous sulfate electrodes. At each step 16 readings could be made to test the reproducibility of the results.

The thermostats were accurately controllable and constant to 0.01°. The hydrogen used in these experiments was prepared by the method of Cooke and Richards.[7] The mercury used was carefully purified and finally treated according to the method described by Hulett.[8] The mercurous sulfate was electrolytically prepared according to the method of Wolff and Waters.[9] The potentials were measured with a Leeds and Northrup potentiometer and a sensitive galvanometer. The Weston standard cell which was used was recently calibrated by the Bureau of Standards.

Before the effect of temperature on a particular electrode was studied, the e.m.f. of the complete cell with both electrodes at 25° was determined to see that the values obtained agreed with those previously reported. For the cell containing sulfuric acid of 0.0009102 mole fraction Randall and Cushman[10] give a value 0.7544 volt which is identical with that obtained in this work for the 0.1 *N* sulfuric acid cells. See Table I. For cells containing *N* sulfuric acid (0.00907 mole fraction) we obtained a

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[7] Cooke and Richards, *Am. Chem. J.*, **10**, 81 (1888).

[8] Hulett, *Phys. Rev.*, **33**, 307 (1911).

[9] Wolff and Waters, *Bur. Standards Bull.*, **3**, 625 (1907).

[10] Randall and Cushman, THIS JOURNAL, **40**, 393 (1918).

value of 0.6955 which is in agreement with the value 0.6960 reported by Randall and Cushman for a cell containing sulfuric acid of 0.009014 mole fraction.

The effect of temperature upon the electrodes of the 0.1 *N* sulfuric acid cell was studied first. To determine the effect of temperature on the hydrogen electrode the mercurous sulfate electrodes were kept at 25° and the hydrogen electrodes were kept at each of several temperatures between 0° and 50° at 5° intervals. At the beginning of a determination the hydrogen electrodes were packed in ice several hours before the 0° readings were made. In all cases the readings were constant for a period of at least 30 minutes before they were recorded. When the temperature of the hydrogen electrodes was changed to a new temperature 5° higher, the e.m.f. values became constant within 30 minutes after the new temperature was reached. The 16 readings at any one temperature agreed within 0.0001 volt, except where otherwise indicated in the table. The data in the columns headed π_1 in Part (a) of Table I indicate the change in the potential of the cell, (Pt), H_2, H_2SO_4 (0.1000 *N*), Hg_2SO_4, Hg, when

TABLE I

VARIATIONS OF POTENTIALS WITH TEMPERATURE

(a) Cell: (Pt), H_2, H_2SO_4 (0.1 *N*), Hg_2SO_4, Hg

Temp., °C.	π_1		π_2		π_3	
	V. obs.	Δ mv.	V. obs.	Δ mv.	V. obs.	Δ mv.
0	0.7601[a]	−0.4	−0.7469	−0.5	0.7545	0
5	.7588	− .4	.7489	+ .1	.7548	+0.3
10	.7579	0	.7500	− .2	.7547	+ .2
15	.7565	[0]	.7513	− .3	.7545	0
20	.7551	0	.7532	+ .2	.7544	− .1
25	.7544	+ .6	.7544	[0]	.7545	[0]
30	.7533	+ .8	.7554	− .4	.7547	+ .2
35	.7518	+ .7	.7568	− .4	.7544[b]	− .1
40	.7498	0	.7580	− .6	.7541[b]	− .4
45	.7489	+ .5	.7597	− .3	.7540[b]	− .5
50	.7465	− .5	.7609	− .5	.7541[b]	− .5
	(b) Cell: (Pt), H_2, H_2SO_4 (1.0 *N*), Hg_2SO_4, Hg					
0	0.7060	−0.3	−0.6880	0	0.6988	−0.2
5	.7042	+ .1	.6895	0	.6984	+ .1
10	.7020	0	.6908	−0.2	.6975	− .1
15	.6995	− .3	.6925	0	.6969	0
20	.6975	− .2	.6942°	+ .2	.6962	0
25	.6955	[0]	.6955°	[0]	.6955	[0]
30	.6935	0	.6969	− .1	.6948	0
35	.6913	+ .1	.6984	− .1	.6938	− .3
40	.6886	− .4	.6997	− .3	.6929	− .5
45	.6860	− .9	.7011	− .4	.6918	− .9
50	.6845	− .2	.7038	+ .8	.6910[b]	−1.0

[a] Temperature 0.3°.

[b] Average deviation ±0.2 mv.

the mercurous sulfate electrode is kept at 25° and the hydrogen electrode is varied from 0° to 50°. It will be noted that the hydrogen electrode becomes more electronegative as the temperature is increased and the temperature coefficient is H_2, H_2SO_4 (0.1 N): : Cons't Ref. dE/dT = —0.000,27. The relation between the potential of this electrode and the temperature is linear within the limits of experimental error. After the observed potentials in each column, the deviations (Δ mv.) from the values calculated from the linear temperature coefficient are given. A point on the curve, usually the potential value at 25°, is considered the point of reference in applying the temperature coefficient and calculating the deviations.

To study the mercurous sulfate electrode the hydrogen electrodes were kept at 25° and the mercurous sulfate electrodes changed in temperature from 0° to 50°. The results obtained are given in the columns headed π_2 of Table I. The observed values were in all cases corrected to one atmosphere partial pressure of hydrogen. Increase in temperature makes the mercurous sulfate electrode also more negative. Its temperature coefficient is almost identical with that of the hydrogen electrode using sulfuric acid of the same strength, namely, Cons't Ref. : : H_2SO_4 (0.1000 N), Hg_2SO_4, Hg; dE/dT = 0.000,28.

Since the temperature coefficients of the two electrodes of the 0.1 N sulfuric acid cell are almost equal, it follows that the temperature coefficient of the complete cell should be small. The third column of potential values indicates the variation in the e.m.f. of the complete cell as the temperature was changed from 0° to 50°. It will be noted that temperature has little influence upon the e.m.f. of this cell.

In a similar manner the effect of temperature on the potentials of the electrodes of the cell, (Pt) H_2, H_2SO_4 (1.0004 N), Hg_2SO_4, Hg, and upon the e.m.f. of the complete cell was studied. These data for the potentials of the hydrogen electrode, mercurous sulfate electrode and the complete cell are given in Part (b) of Table I. The temperature coefficients of the two electrodes were found to be, H_2, H_2SO_4 (1.0 N) : : Cons't Ref.; dE/dT- = —0.000,43, and Cons't Ref. : : H_2SO_4 (1.0 N), Hg_2SO_4, Hg; dE/dT = 0.000,30.

It will be noted that the N sulfuric acid-mercurous sulfate electrode has a temperature coefficient close to that of the hydrogen and the mercurous sulfate electrodes having 0.1 N sulfuric acid as the electrolyte. The normal sulfuric acid hydrogen electrode, however, has a much greater temperature coefficient. Since the hydrogen electrode becomes negative more rapidly than the mercurous sulfate electrode, the single potential values of these electrodes approach each other at higher temperatures and therefore increased temperature should decrease the e.m.f. of the complete N sulfuric acid cell. If the temperature coefficient of the mercurous sulfate electrode is subtracted from that of the hydrogen electrode, a temperature coefficient of —0.000,13 volt per degree for the complete cell is indicated. The data in the last column of Part (b) of Table I are the e.m.f. values of the complete cell at temperatures between 0° and 50°. These data indicate a temperature coefficient of —0.000,14 volt per degree up to 40° which agrees closely with the coefficient calculated from the coefficients of the two electrodes.

The effect of temperature on the two practical hydrogen electrodes studied in this work is quite different from the behavior which Lewis and Randall[6] assumed for the 0.1 *M* hydrochloric acid hydrogen electrode in their derivation of the temperature coefficient of the 0.1 *N* calomel electrode. They use the value, H_2, HCl (0.1 *M*) : : H^+ (*M*), H_2 (Pt); $\Delta E/\Delta T = +0.000{,}22$. The values for the 0.1 *N* and *N* sulfuric acid-hydrogen electrodes were found to be —0.000,27 and —0.000,43, respectively, using a constant reference electrode. The data of Fales and Mudge on the electrodes of the cell, (Pt) H_2, HCl (0.1 *M*), sat. KCl, sat. KCl Hg_2Cl_2, Hg indicate that the temperature coefficient of the 0.1 *M* hydrochloric acid hydrogen electrode is —0.000,70. The differences between the coefficient assumed by Lewis and Randall and those found experimentally may be due to a failure on the part of these writers to consider the change in the activity of the hydrogen ion in the practical hydrogen electrode with temperature, or, what is less likely, to the assignment of an unusual temperature effect to the standard electrode, or to an enormous liquid-temperature junction effect. If a study of the hydrogen electrode in a cell of the type (Pt) H_2, HCl (0.1 *M*), Hg_2Cl_2, Hg which is free from liquid-junction potentials supports the results of Fales and Mudge, a value for the temperature coefficient of the 0.1 *N* calomel electrode will be obtained which is very different from the value now accepted. Preparations have been made for such a study.

Since the sulfuric acid-hydrogen electrodes become more electronegative as the temperature increases, the activity of hydrogen ion in the sulfuric acid solutions must increase so rapidly with temperature as to offset any increase in the e.m.f. of the cell H_2, H_2SO_4 : : H^+ (*M*), H_2 due to increases in the value of *T* in the equation, $E = (RT/nF) \log_n (a_{H^+}/a = 1)$. In this statement the hypothetical standard electrode is considered to have the same potential at all temperatures. In *N* sulfuric acid the activity of the hydrogen ion approaches unity with increased temperature much faster than in 0.1 *N* acid.

Summary

1. A study has been made of two methods which have been used for determining the temperature coefficients of reference electrodes and the results of the two methods have been compared.

2. The method used by Fales and Mudge to determine the temperature coefficient of the saturated calomel electrode has been used to determine

the temperature coefficients of the following electrodes: H_2, H_2SO_4 (0.1 N) : : Constant Reference, $dE/dT = -0.000,27$; H_2, H_2SO_4 (1.0 N) : : Constant Reference, $dE/dT = -0.000,43$; Constant Reference : : H_2SO_4 (0.1 N), Hg_2SO_4, Hg, $dE/dT = +0.000,28$; Constant Reference : : H_2SO_4 (1.0 N), Hg_2SO_4, Hg, $dE/dT = +0.000,30$. All of the electrodes studied become more electronegative as temperature increases.

3. It has been pointed out that an assumption made in the development of the temperature coefficient of the tenth normal calomel electrode that the e.m.f. of the cell, H_2, HCl (0.1 M) : : H^+ (M), H_2, is proportional to the absolute temperature is not supported by the experiments on sulfuric acid-hydrogen electrodes or by those of Fales and Mudge on the 0.1 M hydrochloric acid hydrogen electrode.

4. The fact that sulfuric acid-hydrogen electrodes become more electronegative as the temperature increases indicates that the activity of the hydrogen ion increases with temperature so rapidly as to offset any increase in potential indicated by an increased value of T in the equation $E = (RT/nF) \log_n (a_{H^+}/a = 1)$.

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THE ABSORPTION SPECTRUM AND THE PHOTOCHEMICAL DECOMPOSITION OF ACETONE

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This paper reports a determination of the molal extinction coefficients of gaseous acetone between 3500 Å. and 2000 Å., and rate measurements on the photochemical decomposition of acetone in limited regions of the spectrum. The primary purpose of the work was to determine whether the decomposition is caused by radiation corresponding only to the peak of the curve or if all absorbed energy is effective. The plotting of the absorption curve was a necessary incident. The absorption curves of aqueous and of alcoholic solutions of acetone were known.[1] The curve for gaseous acetone was obtained by the following method.

Oxidized copper gauze screens, of various meshes, were mounted over circular holes (7.5 cm. in diam.) in 15cm. squares of sheet iron. The ratio of the light transmitted by each screen to the total incident light was determined with the aid of a photometer having a bench length of 300 cm. An electric light was mounted at each end, and by adjusting the current in one of them by means of a variable resistance the lamps were made to furnish the same intensity of light. For this adjustment and with no

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[1] Bielecki and Henri, *Compt. rend.*, **155**, 456 (1912); **156**, 884 (1913); *Physik. Z.*, **14**, 515 (1913); *Ber.*, **46**, 3570, 3627, 3650 (1913).