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Absolute half-cell potential: A simple direct measurement

Wilford N. Hansen
Department of Physics, Utah State University, Logan, Utah 84322

Galen J. Hansen
Division of Material Science and Technology, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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The concept of the absolute half-cell potential is discussed from a simple thermodynamic point of view and defined as $-\Delta G/ne$ for the half-cell reaction, treating the electron like other individual chemical species. With the standard reference state of the electron taken as the free electron at rest at infinity, the absolute half-cell potential is simply the *Fermi level of the electrons in the half-cell lead wire*. This potential can be simply measured with a Kelvin probe by determining the vacuum potential level over the electrolyte relative to the Fermi level of the half-cell lead. Since the probe cannot determine potentials absolutely, it must be calibrated using a material whose work function is known. Using this procedure we obtain for the standard hydrogen half-cell, $E_{\text{abs}}(\text{SHE})=4.456\pm0.025$ eV, assuming our Hg as used in calibration has a work function of 4.495 eV.

INTRODUCTION

Over the past two decades a great deal of attention has been given to the subject of the absolute half-cell potential.[1–11] In recent years some authors have taken the preferred value of the half-cell potential (hereafter called E_{abs}) as equal to the Fermi level of the metal electrode minus the vacuum level (i.e., outer potential) of the half-cell solution,[7,8,10] but there is no consensus (e.g., see Ref. 6). In addition, up to now the determination of the value of E_{abs} has usually involved both tedious measurements and theoretical estimates (Refs. 6, 7, and 10–13). Also, the concept of the absolute half-cell potential and its relation to the thermodynamics of the half-cell has not been made clear and simple. There has been much disagreement on subtle but crucial points. Dialogue is still needed to clarify this subject, and especially to reduce it to a few simple essential concepts.

In this paper we wish to show in a clear and concise manner how the absolute half-cell potential E_{abs} is easily derived and conceptualized from a thermodynamic point of view. We consider the half-cell as a separate entity with its own thermodynamics. From this point of view the half-cell potential follows naturally. It is simply the Fermi level in the half-cell lead wire (with sign changes because electrons are negative) when the half-cell is at equilibrium. Thus it can be shown that

$$-E_{\text{abs}}=\frac{\bar{\mu}_{e^-}^{\text{eq}}}{e}$$

is equal to the Fermi level with respect to ϕ_∞ (solution surface large and neutral) where $\bar{\mu}$ is the electrochemical potential and e is the charge on the proton. Recently an approach to the problem from the viewpoint of thermodynamically described equilibrium states of the reaction species has been made by Rockwood.[14]

We will also show that E_{abs} can be determined by a simple thermodynamic measurement of a half-cell at equilibrium, without theoretical estimates or assumptions other than those used in determining the work function of mercury, and we will make that determination.

We will not evaluate in depth the work of previous authors in this paper, nor discuss the extended implications of the concept of E_{abs} as viewed in this paper. Here we wish only to present a simple derivation, conceptual viewpoint, and measurement of E_{abs}.

THEORY

Derivation of the absolute half-cell potential

We begin by considering a half-cell reaction such as

$$ne^- + M^{n+} \xrightarrow{\Delta G} M \ . \tag{1}$$

The treatment is analogous to that used in Latimer's book[15] except that reduction potentials are used instead of oxidation potentials. The Gibbs free-energy change ΔG for this reaction depends on the conditions or states chosen for each of the species. If the reaction has not started toward equilibrium, then these chosen states of the reaction species constitute the "initial" states, and ΔG of Eq. (1) is ΔG^i. The Gibbs free energy of a species G_x will be discussed here in terms of electron volts, and

$$-\Delta G/ne = E \ \ (\text{volts}) \ . \tag{2}$$

For simplicity of nomenclature, the number of electrons in the reaction n will be 1 hereafter. The absolute half-cell potential is simply E of the half-cell reaction with its species in their initial states before equilibrium is allowed to occur.[16–19] That is,

$$\begin{aligned} E_{\text{abs}} &= -\Delta G^i/e \\ &= (G^i_{M^+} + G^i_{e^-} - G^i_M)/e \\ &= (\bar{\mu}^i_{M^+} + \bar{\mu}^i_{e^-} - \bar{\mu}^i_M)/e \ . \end{aligned} \tag{3}$$

Here $\bar{\mu}_x^i$ is simply the electrochemical potential of any chemical species x shown in its initial state, i.e., Gibbs free energy per electron. Equation (3) gives the absolute potential of any half-cell in terms of its initial states before equilibrium. If the initial condition of the reaction species were their "standard" states, e.g., unit activity H^+, then it would seem appropriate to call E_{abs} the absolute *standard* half-cell potential and label it E_{abs}^0.

When the initial, half-cell metal is placed in contact with the initial electrolyte and the half-cell reaction of Eq. (1) goes to equilibrium, ΔG goes to zero. The following simple cycle is useful in our analysis. Labels on the arrows are ΔG (per e^-) in the direction of the arrow. We seek ΔG^i (per e^-), which is equivalent to the absolute half-cell potential (with sign change):

$$\begin{array}{rcccl} & e_i^- + & M_i^+ & \xrightarrow{\Delta G^i} M_i & \text{(initial states)} \\ (\bar{\mu}_{e^-}^{\text{eq}} - \bar{\mu}_{e^-}^i)\downarrow & & \downarrow & \uparrow 0 & \\ & e_{\text{eq}}^- + & M_{\text{eq}}^+ & \xrightarrow{\text{eq}} M_{\text{eq}} & \text{(equilibrium states)}\ . \end{array} \tag{4}$$

Starting with e_i^- and M_i^+ in the upper left we can pass to M_i on the right side by going straight across or through the equilibrium. The metal G_M does not change, and neither does G_{M^+} if we hold the solution inner potential constant. Also across the equilibrium, $\Delta G = 0$. Thus the only change in G by the lower route is in going from e^- (initial state) to e^- (equilibrium) for which ΔG is $(\bar{\mu}_{e^-}^{\text{eq}} - \bar{\mu}_{e^-}^i)$. Thus

$$\Delta G^i = (\bar{\mu}_{e^-}^{\text{eq}} - \bar{\mu}_{e^-}^i)\ , \tag{5}$$

where

$$\Delta G^i = -eE_{\text{abs}}\ .$$

Now if the initial (reference) state for the electron is taken as the electron at rest at infinity with its Gibbs free energy taken as zero,

$$E_{\text{abs}} = -\bar{\mu}_{e^-}^{\text{eq}}/e\ , \tag{6}$$

i.e., *the absolute half-cell potential is simply the Fermi level of the electrons in the half-cell lead wire (with sign reversal using present convention).* If another conductor were available whose Fermi level were well known with respect to ϕ_∞, E_{abs} could be accurately measured with a voltmeter. This is not easily the case, however, and the measurement, while simple in concept, requires careful thought to carry out.

Determination of E_{abs}

Initial states of the half-cell

To help us choose initial states and easily visualize the determination of E_{abs}, a few points need to be discussed. First, let us place in field-free space (perhaps in a Faraday cage or out beyond the solar system) a crystal of the metal M which is neutral, and whose exposed faces are all identical. (This latter condition is relaxed later.) We do the same with a neutral electrolyte of a chosen concentration of M^+, whose surfaces are identical, clean, and have only intrinsic surface dipole layers. Since all the surfaces of the metal and solution are neutral, there are no external fields. Therefore, the vacuum levels (outer potentials) of the metal and the solution, ψ_M and ψ_S, respectively, are the same and are equal to the electrostatic potential at infinity, taken as zero. The electrochemical potential of electrons in the neutral metal and that of the ions in the neutral solution will each have a definite value with respect to zero, namely, $\bar{\mu}_{e^-}^n$ and $\bar{\mu}_{M^+}^n$ (often called the "real" potential of the species). For the electron, $\bar{\mu}_{e^-}^n$ is the negative of the work function for the metal surfaces, $-\Phi_M$.

Actually, our concern for electrical neutrality is only temporary for the thought experiment. It will be relaxed later, because work functions and differences in outer potentials are independent of uniform grounding potential shifts with consequent small surface charge changes.

The Fermi level with respect to infinity, and hence the vacuum level, of a conductor will change as excess charge is placed on it. Thus specifications of the half-cell and its initial conditions, when defining E_{abs}, must include the excess charge. We choose as the initial state of the metal ion, a solution of given concentration of M^+ whose exposed surface is very large with respect to the metal, neutral at large distances from the metal, and clean. Thus, ψ_S will be zero with respect to ϕ_∞. For the metal, we choose a pure metal whose surface of interest is also neutral before contact, and clean. The initial state of the electron is taken to be at rest at infinity. Though later we will see that the measurement of E_{abs} is independent of all excess charges, choosing surface neutrality as the initial and after-contact condition of the solution conceptually allows ψ_S to equal zero, and E_{abs} to be simply the Fermi level of the half-cell lead.

These initial potential levels are shown in Fig. 1. Some additional potential designation are included in Fig. 1 to coordinate with other literature. χ is called the "surface potential," whereas μ_{e^-} is the chemical potential of the electron. A comment on nomenclature is needed here. Some of the conceptual difficulty in the literature, we believe, is caused by confusing nomenclature. There is the matter of electrostatic "potentials" which relate to the energy of unit positive test charges which are imagined never to disturb the system. Then there are electrons (negative charges) which polarize the system (image charges) and interact chemically (chemical potential). Then there is the matter of energy level versus Gibbs free-energy level, often not even distinguished. Using all of these on a single figure can be confusing. In Figs. 1 and 2 the ordinates are electrochemical potentials, i.e., Gibbs free energies (in eV) per electron (e^-) and per metal ion (e^+). The size of the potential unit is thus that of the ordinary volt. In order to keep the nomenclature clear when both negative and positive test charges are used, we will use a small presuperscript "e" to designate when an electron is the test charge. Thus ${}^e\psi_M$ (eV per e^-) $= -\psi_M$ (eV per e^+), etc. It may also be useful to make a point with regard to the electrochemical potential of electrons since some authors seem to have trouble with this concept.

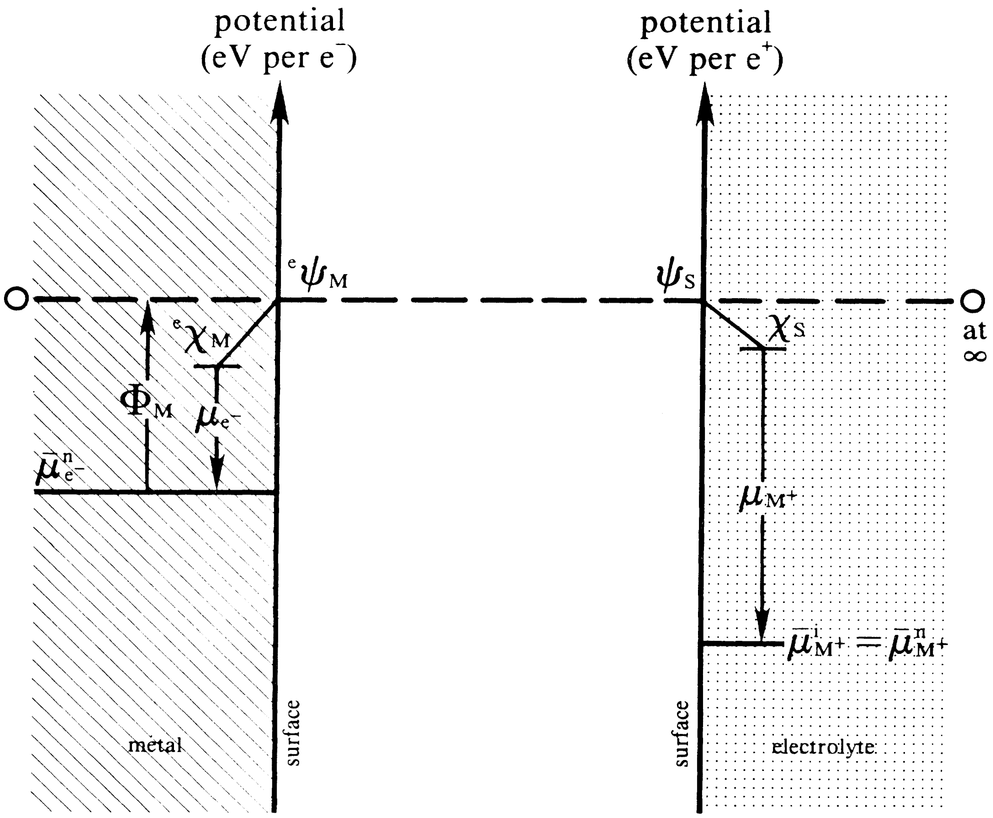

FIG. 1. Half-cell metal and electrolyte in their initial states. Vacuum levels are equal and equal to the potential at infinity, since the surfaces are neutral.

First of all, in an electrode, the electrochemical potential of the electrons and the Fermi level are identical. Secondly, by definition,[20]

$$G = U - TS + PV \ , \tag{7}$$

where U is energy, T is temperature, S is entropy, P is pressure, and V is volume. A group of delocalized electrons with negligible translational energy, at infinity and with negligible group self-energy, is in a perfectly good thermodynamic state. Since S and PV equal zero for such a state, $G = U$. Therefore the change in electrochemical potential (Gibbs free energy) of an electron in free space tracks the change in ordinary electrostatic potential (with change in sign). This means that we can take the electrochemical potential of an electron at rest at infinity as equal to its energy and set it to zero.

In this work we assume that a Kelvin probe measurement can determine the work function. We also assume that photoelectric measurements at temperatures near or below room temperature can be used to determine the work function, even though such measurements are not carried out at thermodynamic equilibrium. The validity of these assumptions is discussed in the Appendix.

Half-cell equilibrium

Now that we have chosen initial states for the half-cell components, let us see what happens when the components are joined and the half-cell equilibrates. First, let us take the electron from infinity (or from $^e\psi_S^i = {^e\psi_M^i} = 0$) and place it at $\bar{\mu}_{e^-}$, the Fermi level of the initial half-cell metal. This requires work equal to $-\Phi_M$ (see Appendix). We then place the neutral face of M in contact with a very large excess of the electrolyte, and allow equilibrium to occur. The electrochemical potential of the ions in solution is held constant by virtue of the large excess solution, which maintains neutrality of the exposed solution far from the electrode. In practice ψ_s could be maintained equal to the potential at infinity, ϕ_∞, for any sized solution, by adjusting a battery between M and ground, and making use of a Kelvin probe. Then

$$\bar{\mu}^{\mathrm{eq}}_{M^+} = \bar{\mu}^i_{M^+} = \bar{\mu}^n_{M^+} \ . \tag{8}$$

Equilibrium is achieved by the formation of a double layer at the metal-solution interphase, which shifts the Fermi level of the metal by $\Delta G^i + \Phi_M$. That is, taking the initial state of e^- at infinity and using Eq. (5),

$$\begin{aligned}\Delta\bar{\mu}_{e^-} &= \bar{\mu}^{\mathrm{eq}}_{e^-} - \bar{\mu}^n_{e^-} = \bar{\mu}^{\mathrm{eq}}_{e^-} - (\bar{\mu}^i_{e^-} - \Phi_M) \\ &= \Delta G^i + \Phi_M \ .\end{aligned} \tag{9}$$

Since Φ_M is constant, $^e\psi_M$ must move up and down with $\bar{\mu}_{e^-}$ in the electrode. Therefore, using Eqs. (9) and (5)

$$\begin{aligned}eE_{\mathrm{abs}} &= -\Delta G^i = -(\bar{\mu}^{\mathrm{eq}}_{e^-} - \bar{\mu}^n_{e^-}) + \Phi_M \\ &= -e({^e\psi^{\mathrm{eq}}_M} - {^e\psi^n_M}) + \Phi_M \\ &= e(\psi^{\mathrm{eq}}_M - \psi^n_S) + \Phi_M = e\Delta\psi_{SM} + \Phi_M \ ,\end{aligned} \tag{10}$$

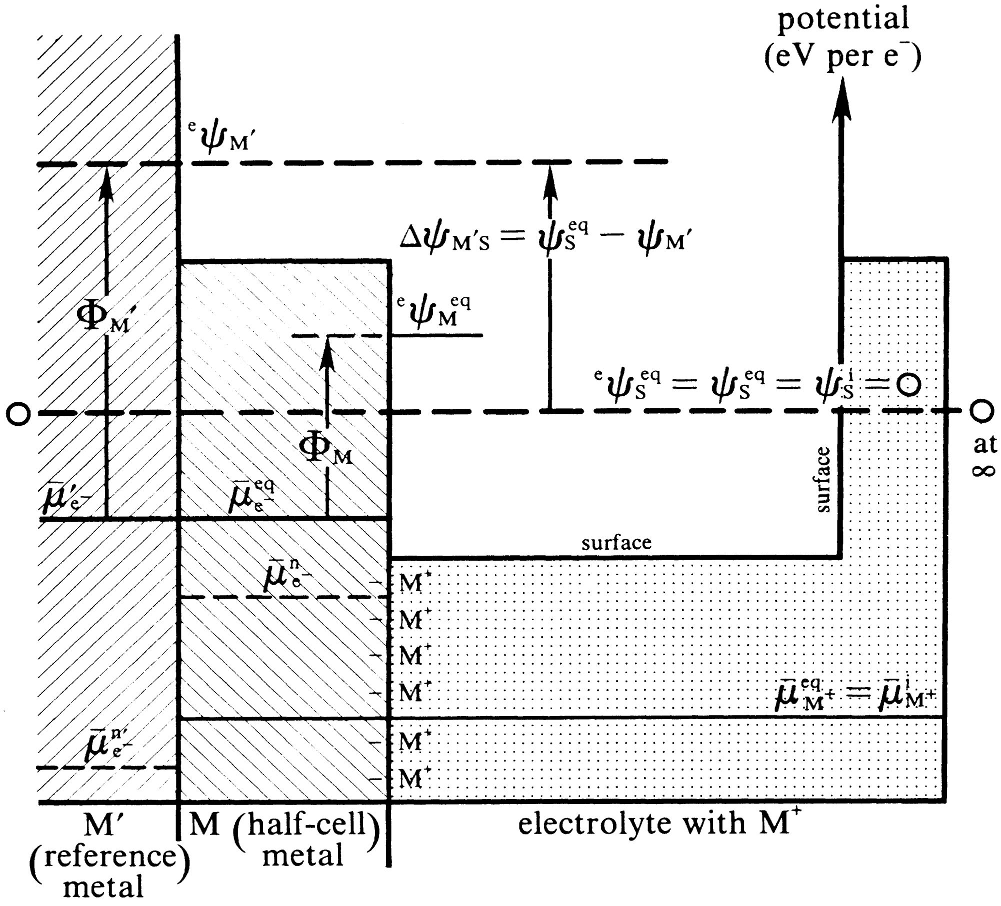

FIG. 2. Half-cell metal in equilibrium with solution. Reference metal is in contact with the half-cell metal so that the Fermi levels are equal. For metal ions the ordinate is eV per e^+. The electrolyte is assumed to be much larger than the metals, ensuring that ψ_S^{eq} is zero.

where $\Delta\psi_{SM} \equiv \psi_M^{eq} - \psi_S^n$.

Measuring E_{abs}

It is now obvious that E_{abs} can be determined by using a Kelvin probe or some other device to measure $\Delta\psi_{SM}$, provided Φ_M is known. The above results at equilibrium are illustrated in Fig. 2. Here we have attached electrically a reference metal M', whose work function $\Phi_{M'}$ is well known, to the half-cell lead. The difference in the neutral Fermi levels of the reference and half-cell metals $\Delta\bar{\mu}_{e^-}^n$ is simply the difference in their work functions $\Delta\Phi_{MM'}$. Since the Fermi levels of the two connected metals are equal to $\bar{\mu}_{e^-}^{eq}$, we can also write E_{abs} as

$$E_{abs} = (\psi_{M'}^{eq} - \psi_S^n) + \frac{\Phi_{M'}}{e} = \Delta\psi_{SM'} + \Phi_{M'}/e \ . \qquad (11)$$

Thus if the half-cell metal is not easily accessible, or does not have a well-known work function, we can use any good reference conductor to determine E_{abs}. The reference metal needs to be connected to the half-cell metal only by a wire, and can be kept physically as far away from the half-cell as desired.

We now make one final relaxation of conditions. Notice that if the vacuum level just outside the electrolyte is changed, say by adding a negative charge to the electrolyte surface such that ${}^e\psi_S^{eq}$ become more positive, equilibrium will insist that all electron potential levels of the half-cell, including the fermi level, rise by the same amount (the double layer is essentially unchanged). Therefore all of the ${}^e\psi$ potentials rise by the same amount, leaving $\Delta\psi_{M'S}$ fixed. $\Phi_{M'}$ is essentially independent of excess charge and does not change. Thus we see that the E_{abs} determination is independent of electrolyte charging [i.e., we can remove the n in Eq. (11)], and we do not require a Faraday cage for the measurement. A cage may help reduce stray fields and thus improve the signal-to-noise ratio. However, in order to relate the determined E_{abs} (independent of excess charge) to the theoretical $E_{abs} = -\bar{\mu}_{e^-}^{eq}/e$ (dependent on excess charge), we must remember that the measured E_{abs} uses ${}^e\psi_S$ as the reference state of the electron, which is theoretically set to zero by battery adjustment if necessary. If one chooses to use ${}^e\psi_S \neq 0$ as the initial state of the electron as Trasatti and others do, E_{abs} can no longer be simply defined as a Fermi level. Keeping $\psi_S = 0$ is only a mental exercise, yet it is a useful concept and does indeed simplify E_{abs}.

EXPERIMENTAL PROCEDURE

As shown above, to determine E_{abs} for a half-cell reaction it is necessary only to make one relative work-function measurement $\Delta\psi_{M'S}$ and to know $\Phi_{M'}$ of the reference metal. The choice of the reference metal is based on how well its absolute work function has already been determined, and especially on how easily it can be prepared in the laboratory without vacuum in a state such that its surface is clean and reproducible. The metal we choose is mercury.

Of great interest is the value of the absolute potential of the standard hydrogen electrode (SHE), E_{abs}. However, in our measurements we use the saturated calomel electrode (SCE) instead of actually using the hydrogen electrode, because it is convenient and its relative half-cell potential with respect to the SHE is well known. The equation for the SCE is

$$e^- + \tfrac{1}{2}\mathrm{Hg_2Cl_2} \rightarrow \mathrm{Hg} + \mathrm{Cl}^- \ . \qquad (12)$$

This half-cell reaction is treated in the same way as Eq. (2). Here Hg and Hg_2Cl_2 always remain in their initial states. Since the ion is negative, the right-hand ordinate in Fig. 1 becomes that for a negative test charge and ψ_S becomes ${}^e\psi_S$.

Measurements were made to determine E_{abs} (SCE) of the saturated calomel electrode at laboratory temperature and pressure. The electrode was a common glass SCE electrode commercially made by Schott and Gen Mainz of Germany. Standard state for the chloride ion was taken to be saturated KCl solution, neutral, and with a clean surface. However, evaporation of the standard solution allowed KCl crystal formation on the solution surface during measurement which cluttered the solution surface, so a 90% saturated solution was used in series, into which the SCE electrode was placed connected by a salt bridge. The difference in KCl concentration between the measured solution and inside the SCE electrode should not change χ_S appreciably.[21] The standard states of Hg and Hg_2Cl_2 were taken to be the pure metal and Hg_2Cl_2 paste found inside the SCE. The reference metal used was triply distilled mercury. Both the mercury and the SCE lead were connected to the reference lead of the Kelvin probe.

The measurement was made inside a nitrogen-purged glove box, and a small stream of high-purity nitrogen was blown over the surface of both the solution and the reference mercury. Stability of the probe was good, with potential drift of only a few mV over the course of the measurement (approximately an hour). $\psi_{M'}$ of the mercury and ψ_S of the solution could be measured to about ±2 meV.

The measurement $\Delta\psi_{SM'}$ was made by first pouring fresh de-aerated solution into a petri dish, in contact with the SCE, and raising the solution to within a millimeter or two of the probe. The probe reading was made within 10–20 sec after the initial pouring of the solution, and other readings made over a period of 2 or 3 min. The solution was then set aside to be measured later. Clean mercury was then poured via a small tube into a clean perti dish, and raised to within a millimeter or two of the probe. Again the first probe reading was made within 10–20 sec after the mercury was poured into the dish, and several more readings taken over the course of a few minutes. The mercury was then removed and the old KCl solution remeasured before fresh solution was again measured. After measuring the solution, the old mercury was remeasured before examining the newly poured mercury. This procedure was repeated several times to observe any drift in the probe, and to obtain an average value for $\Delta\psi_{SM'}$.

RESULTS

In Table I are found the results of the relative work-function difference measurements, $\Delta\psi_{SM'}$, made on three separate days. Table II includes the set of probe readings for $\Delta\psi_{M'}$ and $\Delta\psi_S$, the relative work functions of M' and the solution, for one of the days. The readings were taken over the course of an hour or so. As can be seen, stability of the probe and solution surface are good to ±3 mV (the noise level of the probe). For the mercury $\Delta\psi_{M'}$ at first tended to move in the positive direction in time. After a few minutes, the reading drifted in the negative direction. Its initial reading is thus a function of the time needed to pour out the mercury and raise the surface to the probe, on the order of 30 sec.

Comparing the $\Delta\psi_S$ values measured over solutions of 90 Vol. % and 60 Vol. % we found that any potential error caused by using the 90 Vol. % KCl solution instead of a 100 Vol. % solution was within the noise of the probe.

Using the average value of $\Delta\psi_{SM'}$ from Table I of $+0.203$, and 4.495 as the work function of mercury at room temperature,[4,22,23]

$$E_{\text{abs}}(\text{SCE}) = +4.698 \pm 0.025 \text{ eV} \ . \qquad (13)$$

The value of E(SCE) vs E(SHE) is $+0.242$ eV.[15] Therefore, we obtain as the absolute potential of the standard hydrogen electrode

$$E_{\text{abs}}(\text{SHE}) = +4.456 \pm 0.025 \text{ eV} \ . \qquad (14)$$

This compares favorably with values for E_{abs}(SHE) calculated by Gurevich and Pleskov ($+4.43$ eV),[12] and Reiss ($+4.43$ eV),[10] and is a little below that of Lohmann ($+4.48$ eV).[13] It is well below that Gomer and Tryson ($+4.73$ eV),[6] and Hansen and Kolb ($+4.70$).[24]

CONCLUSIONS

If we write down half-cell reactions in a traditional way, analogous to that done in Latimer's work,[15] and break with tradition by viewing the half-cell by itself and treating the electron like another charged chemical

TABLE I. Determination of E_{abs} for SCE on three separate days (Φ_{Hg} taken as 4.495 eV).

Time	$\Delta\psi_{SM'}$		E_{SCE}
Day 1	$+0.200$	± 0.010	$+4.695$
Day 2	$+0.200$	± 0.010	$+4.695$
Day 3	$+0.210$	± 0.010	$+4.705$

TABLE II. Typical set of measurements between KCl and Hg to determine $\Delta\psi_{SM'}$.

$\Delta\psi_S^{eq}$ Probe reading over 90 Vol. % KCl		$\Delta\psi^{eq}_{M+}$ Probe reading over Hg		
First	10 min later	First	2 min later	10 min later
−0.775	−0.769	−0.572		
−0.775	−0.777	−0.564	−0.571	
−0.777		−0.567	−0.544	−0.682
−0.776	−0.770	−0.583	−0.560	−0.640
−0.775				

species, the "absolute" half-cell potential becomes a simple concept. In this paper, its measurement also has been shown to be simple. The measurement is also direct in that no theoretical estimates are required.

Although care must be taken in preparing the half-cell itself, probably the biggest error in absolute half-cell potential values at the present time is the uncertainty in the absolute work function of mercury. This could be eliminated by choosing the Fermi level of pure neutral mercury (or some other conductor) as the standard state of the electron. Then only relative work-function measurements would be required, they being easier to make and more accurate than absolute work functions. On the other hand, an electron at rest at infinity is an appealing standard state and will probably win out. Actually other procedures are probably more accurate than those used here for determining $\Delta\psi_{SM'}$. Farrell and McTigue[25] claim to determine $\Delta\psi_{SM'}$ between a solution and mercury to stable values of ±0.02 mV. If this is valid and the absolute work function of mercury as they use it were known to that accuracy, absolute half-cell potentials could be accurate indeed.

Several fundamental points should be considered in connection with an absolute half-cell potential as defined here. First, for two half-cells with a common electrolyte (no salt bridge) the whole cell potential will always be simply the sum of the two half-cell potentials. Second, the absolute potential will change a small amount if the χ potential of the electrolyte changes a small amount due to the presence of foreign substances in the surface. Third, when combining two half-cells of different electrolyte, the two half-cell potentials may not add up exactly to the whole unless care is exercised in designing the half-cells. One way to insure that the two half-cell potentials will always add up to that of the whole is to let each half-cell include a salt bridge connection to a third universal electrolyte, and reference all half-cell potentials to the outer potential ${}^{e}\psi^{eq}_{So}$ over the universal electrolyte. Also a final point: The presence of gas ambient instead of vacuum is regarded as having negligible effect on potentials at points away from condensed matter surfaces, except for surface dipole effects. In other words, the gas phases were ignored except for their surface interactions. We believe this to be a valid procedure.

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APPENDIX

Here we discuss possible questions associated with the fact that work-function measurements are not necessarily reversible thermodynamic measurements. For example, does this invalidate using them as we have done?

The "true work function" of a uniform surface of an electronic conductor is defined[26] as the difference between the electrochemical potential $\bar{\mu}$ of the electrons just inside the conductor and the electrostatic potential energy $-e\psi_M$ of an electron in the vacuum just outside it. (For energy expressed in eV, e is unity.) This is equivalent to defining the work function as the difference between the Gibbs free energy per electron of electrons just outside the metal (beyond the image force) and that of electrons at the Fermi level, because outside the conductor $G = U$ for electrons at rest. Now it can be shown[27] that this ΔG is equivalent to the minimum work required to take electrons from the Fermi level to a state of rest just outside the metal. This point is by no means obvious, because the process is not isothermal. However, it permits the work function to be defined as the difference between two free-energy states of electrons. We use this as the working definition of a work function, and by use of a calibrated Kelvin probe can quickly determine the true work function of most any uniform conductor. Note that it is ΔG and not ΔU that is to be determined. Since this is true, the work function can be defined as the difference between two free-energy states of electrons. In this paper we assume that a Kelvin probe measurement between the Fermi level and a position just outside the conductor is a determination of the work function of the conductor, provided the work function of the metallic probe head is known. We also assume that work functions can be determined photoelectrically. We will now give arguments to show that both methods can give the true work function as defined at the beginning of this Appendix.

First consider the Kelvin probe method. Equilibrium is established by biasing the probe with a dc voltage until no ac current flows. It is true that the electrons are not at equilibrium from the sample Fermi level, across the gap, to the probe Fermi level, i.e., $\bar{\mu}_{e^-}$ is not equal in all three regions, even if a low-pressure electron gas exists in the gap. But thermodynamic equilibrium is attained in the sense that $(\partial\bar{\mu}_{e^-}/\partial\chi)_q$ in the probe head is zero at null. Here χ is the displacement of the head and q is the charge on the capacitor made up of the probe head and the sample. Thus the Kelvin probe method is based on thermodynamic equilibrium.

Now let us consider photoelectric determination of the work function, as might be accomplished by observing the voltage for onset of photoelectrons in an XPS or UPS spectrometer. For deep electron energy levels, relaxation of the electron cloud before the ejected electron can get out may affect its energy. But relaxation effects are not important when considering the flood of low-energy electrons that have sufficient energy to just make it out of the metal. These are observed as the onset, whose steep rise is used to determine the work function. Here, even though the electrons have suffered many collisions in the conductor, they are not at thermal equilibrium. The question arises: What is being measured? Evidently it is ΔU and not ΔG that is being measured. In principle they differ. However,the electrochemical potential $\bar{\mu}_{e^-}$ corresponds to the electron energy level that has a probability of $\frac{1}{2}$ of being filled, and this energy lies in the energy region where the probability of occupancy is decreasing rapidly. This is just the energy that can be determined to an accuracy of the order of or better than kT, i.e., $\frac{1}{40}$ eV at room temperature.

From another point of view, it can be shown that it matters very little whether we measure ΔG or ΔU in work-function determinations. Thermodynamic functions of a typical Fermi gas are calculated and presented in Appendix C of Ref. 28. Using these data it can be shown that at 300 K the value of TS for the electrons of a typical metal is very small compared to G. PV is even smaller. Thus G and U typically differ by less than one part per thousand. This implies that only this small error is made where ΔU is used where ΔG is called for.

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