

## Standard potential of hydrogen electrode

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The basis for determination of standard potential of hydrogen electrode is discussed. The EMF values for five cells, each one having a half cell consisting of a hydrogen electrode with different activities/concentrations of hydrogen ions, the other half cell being either Ag/AgCl or An/AnCl<sub>2</sub> of different molalities, are measured using solid ion-transmitting bridge without liquid junctions to calculate thermodynamic activities. It has been concluded that the standard potential of hydrogen electrode is actually zero, as the measured EMF value for the cell Zn/ZnCl<sub>2</sub> (0.6299 m)/HCl (1.18 M)/H<sub>2</sub> (1 atm), Pt viz. -0.762 V is in accordance with the standard potential of zinc obtained from precise calorimetric data. The various factors that support this conclusion are presented.

RECENTLY it has been demonstrated that it is possible to measure single ion activities using a solid chloride ion transmitter bridge-AgCl bridge. Single ion activities of zinc and chloride in ZnCl<sub>2</sub> solutions in molality range 0.1-0.001 were reported<sup>1</sup>.

Measurement of single ion activities should lead to determination of absolute electrode potentials. The assumption made for arriving at the standard potentials of various electrode system is that the standard potential of hydrogen electrode is zero. Precise calorimetric data for standard potential of zinc, which is not dependent on any potentiometric value, are available. It should, therefore, be possible to determine the standard potential of the hydrogen electrode using half cell potentials of zinc electrode reported earlier and the standard hydrogen electrode.

The hydrogen electrode used for the potential measurement was equipped with a presaturator, a hydrogen bypass and was designed to be completely immersed in thermostatted bath. The cell set up is described elsewhere<sup>2</sup>. The two hydrogen electrodes were platinized from a solution of 1% chloroplatinic acid containing 10 mg lead acetate with a current density of 30 mA/cm<sup>2</sup> for 10 min. The electrodes were then rinsed with distilled water several times.

For the preparation of solid-ion transmitting bridge, pure AgCl was melted into the bridge in the form of a 'U' tube made from pyrex glass with a capillary of 2 mm bore diameter. The tubes are then heated to 380°C and held at that temperature for 10 h and then allowed to cool.

Table 1. Mean activity coefficient of HCl at 25°C

Molality	Activity coefficient	Molality	Activity coefficient
0.001	0.966	0.5	0.769
0.005	0.930	1.0	0.811
0.01	0.906	1.5	0.898
0.05	0.833	2.0	1.011
0.1	0.798	3.0	1.31

The hydrogen electrode was immersed in water in a thermostat set to 25°C. The thermostat is a Haake D8, Germany capable of controlling the temperature by ±0.1°C. Pure hydrogen is passed to the cell by Hydrogen Generator model No. 8200 of Packard Instrument Company, Canberra.

It is reported by Vogel<sup>3</sup> that a solution of 1.18 M corresponds to unit activity and is supported by literature values<sup>4</sup>.

From Table 1, it can be seen that 1.0 m corresponds to an activity of 0.811 and 1.5 m corresponds to an activity of 1.347. So an activity of 1.00 corresponding to molarity of 1.18 m follows from interpolation. Molarity of 1.18 corresponds to an activity coefficient of 0.8475. The modified Debye-Hückel equation (Davies equation) which would give the above mentioned activity coefficient is:

$$-\log \gamma_{\pm} = 0.509 Z_+ Z_- \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3221 \right\}.$$

This equation is acceptable as the empirical constant 'C' for highly concentrated solutions can vary between 0.3 and 0.4 in the formula proposed by Davies<sup>5</sup> for activity coefficient as:

$$-\log \gamma_{\pm} = 0.509 Z_+ Z_- \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} - CI \right\}.$$

Hence we chose the value of 1.18 M for preparing a HCl solution of unit activity.

The exact molarity was determined by standard titration technique. The HCl solution of 0.01 m was prepared by diluting the standard volumetric solution supplied by E. Merck India Ltd. Zinc chloride solutions were prepared by dissolving the exact weights of pure zinc in 1:1 HCl, evaporating to dryness and adding the requisite amount of de-ionized water.

If the activity of a solution of zinc chloride is assumed to be 1,

$$a_{\text{ZnCl}_2} = 4m^3 \gamma_{\pm}^3 = 1,$$

Robinson and Stokes<sup>6</sup> showed that if mean molality and the mean activity coefficient is 1, molality of zinc ion would be  $m_{\text{Zn}^{2+}} = (4)^{-1/3} = 0.6299$  m. In this high molality range, neither the Debye-Hückel equation nor the Guntelberg equation will be applicable. Only the em-

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irical equation proposed by Davies is applicable. The single ion activity of  $Zn^{2+}$  ion will be equal to 1 from the expression

$$a_{Zn^{2+}} = 4m_{Zn^{2+}} \gamma_{Zn^{2+}}$$

Since  $ZnCl_2$  solutions were prepared with extreme care, the molality variation is ruled out and we have prepared a solution 0.6299 m  $ZnCl_2$  to provide for unit activity of zinc ion corresponding to the standard state. This corresponds to an empirical constant  $C$  well within the range of 0.2 to 0.3 in the Davies equation, as in the case of HCl solution. Zinc chloride solution of 0.1 m was also prepared by the above procedure.

The instrument used for potential measurement was ORION expandable ion analyser, model No. EA 940, from ORION Research Inc., USA which is capable of handling signals from high resistance sources with negligible IR drop.

The bridges are tested by interconnecting Tacussel Calomel electrode in saturated KCl and Tacussel Ag/AgCl electrode also in saturated KCl in two different beakers, i.e. the cell



The potential was seen to be in keeping with the expected value of 45.6 mV<sup>7</sup>.

The hydrogen electrodes were tested by observing the potential of the following cells:

1. Pt, H<sub>2</sub> (1 atm), HCl (0.01M)/AgCl, Ag
2. Pt, H<sub>2</sub> (1 atm), HCl (1.18M)/AgCl, Ag

The observed potentials were 464.8 mV and 222.4 mV (standard potential for Ag/AgCl electrode) respectively and were found to be in accordance with values reported elsewhere<sup>8,9</sup>.

It was considered necessary to test the bridge when one of the solutions was acidic as it is well known that the mobility of protons is much higher compared to other ions. For this, the bridge was tested by verifying the potential of the cell



The observed potential agrees with the standard potential of 222.4 mV for the silver-silver chloride electrode.

Table 2. Measured potentials using hydrogen electrode at 25°C

Cell assembly	Potential mV
Pt, H <sub>2</sub> (1 atm), HCl(0.01 m)/Bridge/KCl(s), AgCl, Ag	318.0
Pt, H <sub>2</sub> (1 atm), HCl(0.01 m)/Bridge/ZnCl <sub>2</sub> (0.1 m), AgCl, Ag	409.5
Zn, ZnCl <sub>2</sub> (0.1 m)/Bridge/HCl(0.01 m), H <sub>2</sub> (1 atm), Pt	671.9
Pt, H <sub>2</sub> (1 atm), HCl(1.18 M)/Bridge/KCl(s), AgCl, Ag	199.0
Zn, ZnCl <sub>2</sub> (0.6299 m)/Bridge/HCl(1.18 M), H <sub>2</sub> (1 atm), Pt	-762.0

In order to determine the absolute potential of the hydrogen electrode, the potential of the following cells were measured and the measured potentials are given in the Table 2.

From the potential measured for cell 1 of 318 mV, if we deduct the well-established reference-electrode potential of 199 mV, we arrive at Pt, H<sub>2</sub>(1 atm), HCl(0.01 m) potential of the single electrode system as -119 mV. This half cell is coupled with Ag/AgCl system with 0.1 m  $ZnCl_2$  using the chloride ion transmitter bridge in cell 2. The measured potential of cell 2 is 409.5 mV. Subtracting the hydrogen electrode potential gives a value of 290.5 mV for Ag/AgCl,  $ZnCl_2$ (0.1 m) half cell, which is in accord with the earlier measurements reported<sup>1</sup>.

The potential of cell 3 was measured and was found to be 671.9 mV., i.e. coupling of the same hydrogen electrode with zinc electrode in 0.1 m  $ZnCl_2$  solution through the bridge. Addition of the hydrogen electrode potential gives the potential of the zinc half cell, Zn,  $ZnCl_2$ (0.1 m) as -791 mV which is in accordance with values reported earlier. These data confirm the consistency of the potential measurements made with solid-ion transmitting bridge in acidic systems.

The zinc system was chosen because it is perfectly reversible with respect to the cation, does not form unipositive ions, does not undergo self corrosion, is highly reproducible and precise calorimetric values are available for enthalpy changes<sup>10-12</sup> which when coupled with entropy data, can lead to the standard potential of zinc from methods other than potentiometric methods (See Figure 1). But the final confirmation can come only from direct measurement from a solution of H<sup>+</sup> ions of unit activity.

The potential of the hydrogen electrode system dipping into a solution of unit H<sup>+</sup> ion activity was connected through a solid-ion transmitting bridge to a saturated KCl solution in which Ag/AgCl electrode was dipped (see cell 4, Table 2). The measured potential of 199 mV is in keeping with the expected value.

When the electrode is again dipped into a solution of unit H<sup>+</sup> ion activity and is coupled to a  $ZnCl_2$  solution in which the activity of zinc ion is kept unity (See cell 5 Table 2), the voltage observed is -762 mV which is in accordance with the value derived from calorimetric measurements.

The experimentally observed standard potential of zinc using a solution of unit activity with respect to a zinc ion and HCl solution of unit activity with respect to hydrogen ion is surprisingly in agreement with the calorimetrically determined standard potential of zinc (see Table 2). This shows that standard potential of hydrogen electrode is not an arbitrary zero but is actually zero.

The potential of standard hydrogen electrode is conventionally taken as zero at all temperatures, when the partial pressure of H<sub>2</sub> is one atmosphere and the activity

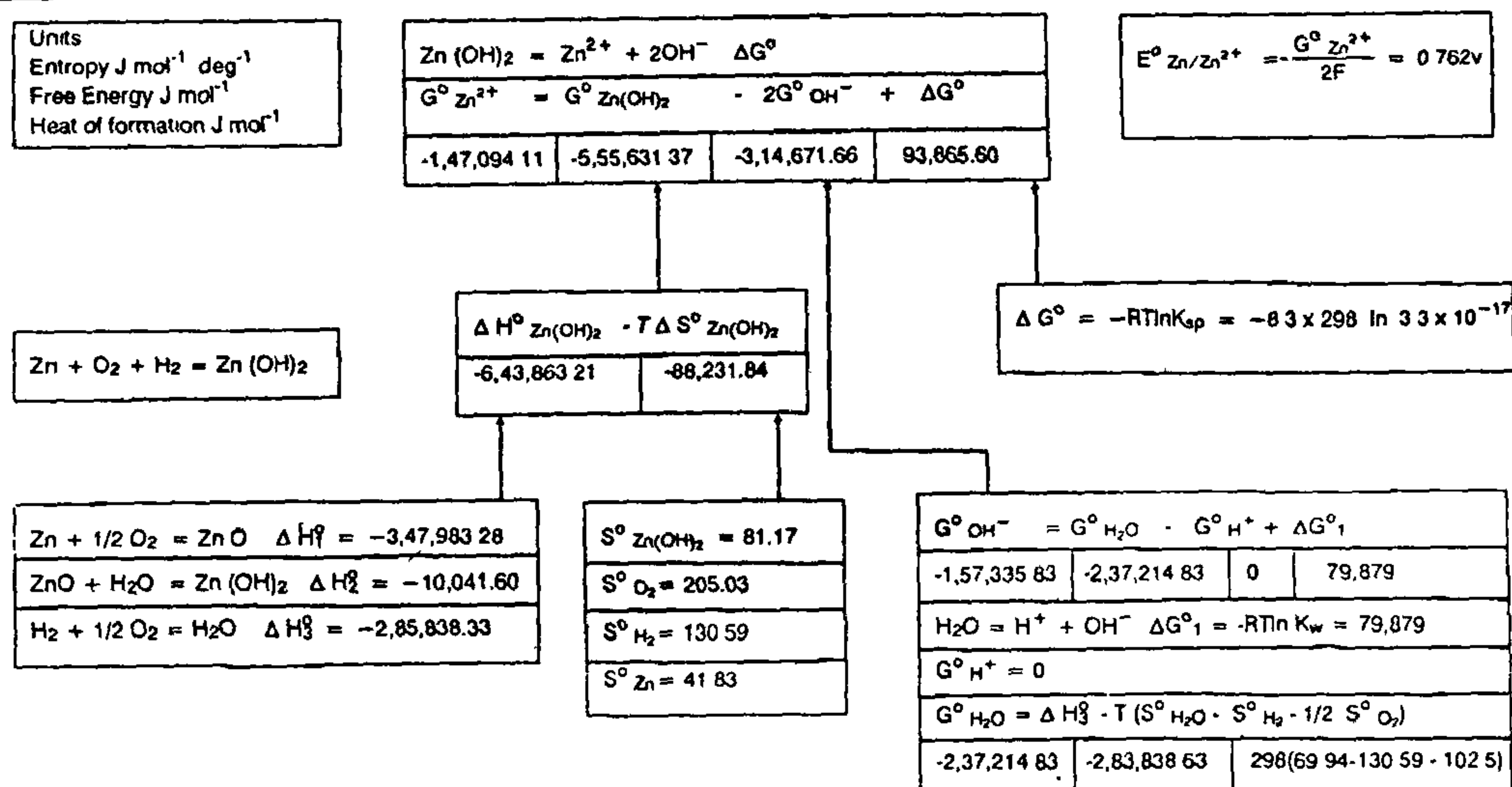


Figure 1. Standard potential of zinc.

of hydrogen is unity. The assumption that the  $E^\circ_{H^+/H_2}$  is zero, leads to the consequent result viz.  $\Delta G^\circ = 0$  which means that the free energy of reactant and product of the reaction



is equal. The possibility of such a situation can be easily understood if one can take into consideration the following facts:

1. Proton, unlike other ions, is of Fermi dimensions ( $10^{-13}$  cm)—a Fermion. It is an elementary particle and is a nonconformist ion<sup>13</sup>. Classical theories are not applicable and quantum-mechanical considerations are possible.

2. The classical thermodynamic considerations are not applicable to fundamental particles like electron, proton etc. Therefore, the question of considering the entropy of the electron of the hydrogen atom which on de-electronation will get mingled with conductance or fermi lectrons of platinum, does not arise.

3. Proton's affinity for electron can be seen from the high ionization energy required i.e. 313 k cal.mole<sup>-1</sup> for removal of an electron from hydrogen atom<sup>14</sup>.

4. The heat of formation of hydronium ion  $H_3O^+$  is 170 k cal.mole<sup>-1</sup> which is considerably less than the ionization energy of hydrogen atom<sup>15</sup>.

5. It is suggested that proton most probably exists in solution as  $H_3O^+$  ions but the evidence is not all that certain<sup>16</sup>.

6. Platinum serves not merely as an insert conductor but functions more as an efficient electrocatalyst<sup>17</sup> enabling the hydrogen molecule to dissociatively adsorb on the surface and help in the de-electronation of hydrogen atom and electronation of proton. The potential of platinum does not influence the hydrogen electrode potential. Large surface area can also be created<sup>18</sup>.

7. The electrical double layer model of Bockris, Devanathan and Muller, which has been accepted as the one that explains many of the observed facts, envisages a layer of water molecules which are highly oriented and has probably a dielectric constant of 6–7 corresponding to a saturated dielectric<sup>19</sup>. The potential of zero charge for Pt in the presence of hydrogen in  $H_2SO_4$  solution is reported<sup>20</sup> to be in the range +0.11 to +0.27 Vs standard hydrogen electrode. At the potential of zero charge, the water molecules are arranged with oxygen end and hydrogen end pointed towards the metal surface in an alternate manner to make the contributions of water molecule to the charge as zero. At the potential of standard hydrogen electrode, viz. zero which will be negative to the potential of zero charge, the charge on the Pt surface will be -ve and therefore the water molecules are adsorbed with their hydrogen ends toward the Pt surface. The presence of hydrogen ends adjacent to Pt surface will not enable hydrogen ion to form hydronium ion. As a result of this arrangement hydrogen ions coming out of the platinum surface due to the de-electronation reaction will remain close to the surface (on the metal side) without forming a hydronium ion.

8. From quantum mechanical considerations, proton mobility has been explained on the basis of proton tunneling as proton is a fermion and classical theories cannot be applied<sup>21</sup>. It has been further suggested that proton jump can occur only if the acceptor water molecules orient so that the oxygen, the proton and the unshared electron of the acceptor electron line up. The two processes, proton transfer and water re-orientation involve a time of  $10^{-14}$  and  $2.4 \times 10^{-13}$ s respectively. In the present case, viz. hydrogen electrode having platinum as the inert electrode, the exchange reaction is the electronation of hydrogen ion to give hydrogen atom and de-electronation of adsorbed hydrogen atom to give a pro-

ton. Both these reactions can be expected to take place at such times, probably, shorter than  $10^{-14}$  s. Which is the time required for proton transfer. The proton, formed as a result of de-electronation of hydrogen atom on Pt surface, remains without forming hydronium ion due to the reason mentioned above, close to the platinum surface and is readily available for electronation reaction. The electrons formed due to de-electronation of hydrogen atoms absorbed on the metal surface can become members of the conductance of Fermi electrons of the metal. The electronation of the proton (or hydrogen ion) and de-electronation of hydrogen atom is most probably occurring on the electrode surface and close to the inner Helmholtz plane of the electrical double layer populated by highly oriented water molecules. This exchange reaction is almost a solid state reaction and takes place at very high exchange rates that is necessary for a standard reference electrode. Thus the forward and reverse (or backward) reaction, viz.  $H^+ + e \rightleftharpoons H$ , can take place with zero free energy change i.e.  $\Delta G^\circ = 0$  and consequently  $E^\circ$  which is given by  $-\Delta G^\circ/nF$  is also zero.

The finding provides a solid base for the electrochemical series built up on the intuitive assumption of W. Nernst that the standard potential of hydrogen can be assigned a value of zero.

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## Selective denaturation of cytochrome c oxidase by ionic surfactants: Depletion of both the heme *a* residues from the enzyme

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**UV-visible absorption and circular dichroism studies on interaction of ionic surfactants with bovine heart cytochrome c oxidase have been carried out in lauryl maltoside solution. Results showed that addition of the surfactant causes irreversible depletion of heme *a* from cytochrome *a* as well as cytochrome *a*<sub>3</sub> sites of this membrane protein at physiological pH. This selective denaturation by ionic surfactants is different from the effect of guanidine hydrochloride on this enzyme. Depletion of heme *a* causes complete inactivation of this ubiquitous respiratory enzyme.**

IONIC surfactants, such as sodium dodecyl sulphate (SDS), are commonly used for denaturation of proteins<sup>1–4</sup>. There has, however, yet been no report on any systematic study on the nature of interaction of surfactants with heme proteins. Moreover, cationic surfactants were considered to be less efficient in such denaturation of proteins, which has been disputed recently<sup>5</sup>, lending it subject for further investigation. We have recently shown that surfactants, both cationic and anionic, can cause release of heme-NO species from nitric oxide complex of myoglobin<sup>5</sup>. Previous studies have shown that membrane proteins are generally more resistant to denaturation than other proteins. Cytochrome c oxidase (CcO, EC 1.9.3.1) is a mitochondrial membrane protein<sup>6–11</sup> with two heme *a* active sites, strongly ligated to one or two histidines of the protein. This enzyme is generally extracted in active form in neutral surfactants such as lauryl maltoside (LM), Triton X-100 (TX-100), etc. Structure and function of this multifunctional enzyme is a subject of frontier interest in recent years. The present report shows that the highly buried heme *a* groups of this enzyme can indeed be depleted by treatment with both cationic surfactant, cetyl trimethyl ammonium bromide (CTAB) and anionic surfactant, SDS, in lauryl maltoside solution. The biochemical effect of surfactants is a subject of growing concern and the present study demonstrates their fatal effect on this vital respiratory enzyme. Furthermore, this study provides an