Fuel cell Fundamentals & Technology Course Code MS/Phy-515
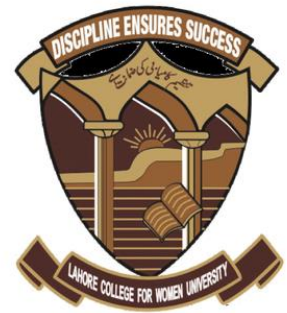
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Derivation of Nernst equation or derive the expression of the effect of pressure (P) and gas concentration (n) on the efficiency (ε) of the fuel cell.

For fuel cell, Gibbs free energy (ΔG_f) value varies with temperature during chemical reaction. But (ΔG_f) changes with reactant pressure and concentration is more important and complex. Consider a general reaction such as:

$$jJ + kK = mM \dots\dots \quad (1)$$

Where j moles of J react with k moles of K to produce m moles of M.

Activity of fuel cell:

The activity of the fuel cell is denoted by **a**. Each of the reactants, and the products, has an associated 'activity'. While a, a_J, and a_K being the activity of the reactants, and a_M the activity of the product.

Cases of activity

1. Ideal gas:

In the case of gases behaving as 'ideal gases', it can be shown that:

$$Activity\ a = P/P^O \ \ldots\ldots\ (2)$$

It is clear that activity is proportional to partial pressure.

where P is the pressure or partial pressure of the gas and P^O

is standard pressure, 0.1MPa.

2. Dissolved Chemicals:

In the case of dissolved chemicals, the activity is linked to the molarity (strength) of the solution. The case of the water produced in fuel cells is somewhat difficult, since this can be either as steam or as liquid.

- For steam, we can say that:

$$Activity = a_{H2O} = P_{H2O} / P^{\circ}_{H2O} \ \ldots\ldots..\ (3)$$

where P°_{H2O} is the vapour pressure of the steam at the given temperature.

▸ **<u>For liquid water:</u>**

In the case of liquid water product, it is a reasonable approximation to assume that $a_{H2O} = 1$.

<u>Gibbs Free energy (ΔG_f)</u>

The activities of the reactants and products modify the Gibbs free energy change of a reaction. Gibbs free energy can be written as:

$$g = h - TS \ \dots\dots \ (4)$$

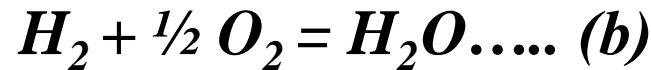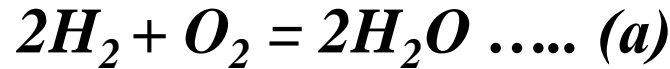$$S\,(T,\,P) = S°(T) - R\,ln\,(P/P_{ref})$$

$$\Delta \overline{g}_f = \Delta \overline{g}_f{}^0 - RT\,\ln\left(\frac{a_J^j \cdot a_K^k}{a_M^m}\right) \quad \dots\dots \ (5)$$

where $\Delta g_f°$ is the change in molar Gibbs free energy of formation at standard pressure.

3. Hydrogen fuel cell:

In the case of the hydrogen fuel cell reaction it can be written as:

$$2H_2 + O_2 = 2H_2O \ ..... \ (a)$$
$$H_2 + \tfrac{1}{2} O_2 = H_2O ..... \ (b)$$

The equation (5) becomes:

$$\Delta \bar{g}_f = \Delta \bar{g}_f{}^0 - RT \ln \left(\frac{a_{H_2} \cdot a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right) \qquad ...... \ (6)$$

▸ **Activity of reactant :**

If the activity of the reactants increases, Δg_f becomes more negative, that is, more energy is released.

▸ **Activity of product**

On the other hand, if the activity of the product increases, Δg_f increases, so becomes less negative, and less energy is released.

Electromotive force (emf) of Hydrogen fuel cell

As the electromotive force (emf) or reversible open circuit voltage of hydrogen fuel cell is:

$$E = \frac{-\Delta \bar{g}_f}{2F} \quad \dots\dots(c)$$

Now, put the value of Δg_f from equation (6) to equation (c) and by expanding we get:

$$E = \frac{-\Delta \bar{g}_f{}^0}{2F} + \frac{RT}{2F} \ln \left(\frac{a_{H_2} \cdot a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right)$$

$$= E^0 + \frac{RT}{2F} \ln \left(\frac{a_{H_2} \cdot a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right) \quad \dots\dots(7)$$

Where E^0 is the EMF of hydrogen fuel cell at standard pressure and is called Nernst equation. The EMF calculated from such equations is known as the 'Nernst voltage' and is the reversible cell voltage that would exist at a given temperature and pressure.

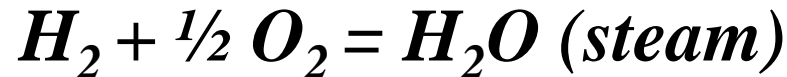## **Logarithmic expression**

The logarithmic function involving the reactants allows us to use the regular rules of the logarithmic functions such as:

$$\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b) \qquad \text{and} \qquad \ln\left(\frac{c^2}{d^{\frac{1}{2}}}\right) = 2\ln(c) - \frac{1}{2}\ln(d)$$

Example of Nernst equation

This makes it straightforward to manipulate equation 7 to get at the effect of different parameters. For example, in the reaction

$$H_2 + \tfrac{1}{2} O_2 = H_2O \ (steam)$$

at high temperature (e.g. in a solid oxide fuel cell (SOFC) at (1000 degree) we can assume that the steam behaves as an ideal gas, and so:

$$a_{H_2} = \frac{P_{H_2}}{p^0}, \qquad a_{O_2} = \frac{P_{O_2}}{p^0}, \qquad a_{H_2O} = \frac{P_{H_2O}}{p^0}$$

now put these values in equation (7)

$$E = E^{\circ} + \frac{RT}{2F} \ln \left(\frac{\frac{P_{H_2}}{P^o} \cdot \left(\frac{P_{O_2}}{P^o} \right)^{\frac{1}{2}}}{\frac{P_{H_2O}}{P^o}} \right)$$

If all the pressures are given in bar, then $P^{\circ} = 1$ and the equation simplifies to

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \right) \quad \text{...... (8)}$$

If the system pressure is P, then we can say that:

$$P_{H_2} = \alpha P$$

$$P_{O_2} = \beta P$$

$$P_{H_2O} = \delta P$$

Where α,β, and δ are constants depending on the molar masses and concentrations of H_2, O_2 and H_2O. By putting and expanding these values in equation (8)

$$E = E^0 + \frac{RT}{2F} \ln\left(\frac{\alpha \cdot \beta^{\frac{1}{2}}}{\delta} \cdot P^{\frac{1}{2}}\right)$$

$$= E^0 + \frac{RT}{2F} \ln\left(\frac{\alpha \cdot \beta^{\frac{1}{2}}}{\delta}\right) + \frac{RT}{4F} \ln(P)$$

These equation provide a theoretical basis and a quantitative indication for a large number of variables in fuel cell design and operation.

Nernst Equation Analysis

The Nernst equation analysis involves:
1) Hydrogen partial pressure
2) Fuel and oxidant utilization
3) System pressure

1. Hydrogen Partial Pressure

In fuel cell, hydrogen can either be supplied pure or as part of a mixture.

$$H_2 + \tfrac{1}{2} O_2 = H_2O$$

If we isolate the pressure of hydrogen term in equation 8, we have:

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \cdot \right) + \frac{RT}{2F} \ln(P_{H_2})$$

So, if the hydrogen partial pressure changes, say, from P1 to P2 bar, with P_{O2} and P_{H2O} unchanged, then the voltage will change by:

$$\Delta V = \frac{RT}{2F} \ln(P_2) - \frac{RT}{2F} \ln(P_1)$$

$$= \frac{RT}{2F} \ln\left(\frac{P_2}{P_1}\right)$$

The use of H_2 mixed with CO_2 occurs particularly in phosphoric acid fuel cells, operating at about $200°C$. Substituting the values for R,T, and F gives:

$$\Delta V = 0.02 \ ln \ (P_2/P_1) V \ldots(9)$$

This agrees well with experimental results, which correlate best with a factor of 0.024 instead of 0.020 .

2. Fuel and oxidant utilization

As air passes through a fuel cell, the oxygen is used, and so the partial pressure will reduce.

The proportion of fuel reduces and reaction products increase. So, we can say that α and β decrease, whereas δ increases. All these changes make the term:

$$\frac{RT}{2F} \ln \left(\frac{\alpha \cdot \beta^{\frac{1}{2}}}{\delta} \right)$$

Smaller and the EMF will fall.

The term RT in the equation shows that drop in Nernst voltage due to fuel-utilization will be greater in high-temperature fuel cells. To obtain high system efficiency, the fuel utilization should be as high as possible.

3. System pressure

The EMF of a fuel cell is increased by the system pressure according to the term:

$$RT/4F \ln (P)$$

So, if the pressure changes from P1 to P2 there will be a change of voltage:

$$\Delta V = \frac{RT}{4F} \ln \left(\frac{P_2}{P_1} \right)$$

Where
- P_2 is the final pressure of the system
- P_1 is the initial pressure of the system

▸ Thank You