Thermodynamics of Fuel Cells

The first law of thermodynamics

“Energy may neither be created nor be destroyed, but may be converted from one form to another.”

\[ \text{dE} = \delta Q - \delta W \]  (1)

Upon Integration

\[ \Delta E = Q - W \]  (2)

\( E \) - system energy

\( Q \) and \( W \) - heat input into the system and the work done by the system respectively

Types of systems

Open system:
Permits both mass and energy transfer

Closed system:
Permits only energy transfer

Isolated system:
Permits neither mass nor energy transfer through its boundaries

A fuel cell is an open system, which permits the flow of mass and energy through its boundaries.

Fuel cell as a control volume

Work is obtained from the transport of electrons across a potential difference and not from mechanical means.

Open systems

Energy change equation for an open system

\[ \Delta E = \Delta U + \Delta KE + \Delta PE + \Delta (PV) \]  (3)

\( U \) - internal energy of the system

\( KE, PE \) - kinetic & potential energies

\( PV \) - pressure-volume work
Enthalpy

Enthalpy (H) combines the internal energy and the PV work terms

\[ H = U + PV \]  (4)

Enthalpy – measure of total system energy

Energy change in an open system

Combining equations 2, 3 and 4:

\[ \Delta H = Q - W \]  (5)

valid only for steady flow conditions, where \( \Delta KE \) and \( \Delta PE \) = 0

Reaction in a fuel cell

Fuel + oxidant = products  (6)

- General reaction in a fuel cell
- Reaction accomplished electrochemically
- Involves transfer of electrons between electrodes

Faraday’s constant

- For each equivalent of chemical change: 
  \(- 6.023 \times 10^{23} \) [Avogadro’s number (A)] electrons are transferred
- Corresponding electricity – given by:
  \[ F = A e \]  (7)
  e - unit electronic charge (1.6 \times 10^{-19} C)
- F (Faraday’s constant) = 96493 Coloumbs / eqv.

NOTE – this value is for a single equivalent of chemical change

Amount of electricity transferred

- No. of electrons transferred during reaction
  Fuel + oxidant = products  (6)
  depends on no. of equivalents of change (N)
- N is obtained from reaction stoichiometry
- Applying Eqn. 7, amount of electricity transferred during reaction is given by:
  \[ \text{Electricity} = N F \]  (8)
- Eqn. 8 gives the amount of electricity transferred by the reaction

Work done by the fuel cell

Electricity = N F  (8)

- This amount of electricity transferred corresponds to a certain amount of electrical work being done by the cell
  \[ W = NFE \]  (9)
- E Cell voltage – difference in potential between electrode terminals
Another expression for work
• Work can also be described in terms of voltage, current and time
  \[ W_e = \int_{t_0}^{t} E I dt \] (10)
• NF has units of charge (C). Current (I) is the rate of flow of charge
• Note that \(E \times I\) has units of power – i.e. work/time – this will be referred to in later lectures

Mathematical statement of the first law in a fuel cell
\[ \Delta H = Q - W \] (5)
Energy change in open systems
\[ W_e = NFE \] (9)
Electric work done in a fuel cell
In the absence of other work, we have:
\[ \Delta H = Q - NFE \] (11)
This is the mathematical statement of the first law for a fuel cell

Second law of thermodynamics
• The first law does not impose any restrictions on the direction of energy transfer
• It considers the energy content of work and heat to be equivalent
• Untrue - it is very difficult to convert heat efficiently to work – while the reverse is very much possible
• Need for second law

Statement
i. No apparatus can operate in such a way that its only effect on the system and surroundings is to convert heat absorbed by a system completely to work done by the system (or) it is impossible by a cyclic process to convert the heat absorbed by a system completely into work done by the system
ii. No process is possible that consists solely in the transfer of heat from one temperature level to a higher one.

Reversible change
• The second law does not proscribe the conversion of heat to work. However, it places a limit on the fraction of heat that may be converted to work.
• The direction of energy transfer is better defined

• Concept of reversibility - fundamental to the second law of thermodynamics

A system is said to undergo a reversible change if it remains in equilibrium as it passes from its initial state to its final state
• Reversible change – easy to visualize in an electrochemical cell – perfect electrochemical apparatus
Perfect electrochemical apparatus
Defined by Gibbs

“If no changes take place in the cell except during the passage of current, and all changes which accompany the current can be reversed by reversing the current, the cell may be called a perfect electrochemical apparatus”

An ideal fuel cell is a perfect electrochemical apparatus

Entropy

- Measure of the disorder in a system
- Defined by the second law
- Irreversible processes generate entropy by:
  - frictional heat loss
  - heat transfer through a finite temperature difference
- Mathematically expressed as:
  \[ dS = \frac{dQ}{T_{rev}} \] (12)

\( S \) – entropy
\( Q \) – heat
\( T \) - temperature

Mathematical expression of the second law

\[ \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \geq 0 \] (15)

- equality applies for reversible processes
- inequality applies for irreversible processes
- Irreversible processes - entropy calculated by assuming series of reversible processes having same initial and final points - approach valid as entropy is a state function

Application of the second law to fuel cells

From equation 11, we have the mathematical statement of the first law for fuel cells:

\[ \Delta H = Q - NFE \] (11)

Applying the second law

\( Q = T \Delta S \) for a reversible system (from eqn. 14)

Therefore,

\[ \Delta H = T \Delta S - NFE \] (16)

The Gibbs free energy (G)

Writing eqn. 16 in differential form:

\[ dH = T dS - FEDN \] (17)

Since the cell is operating reversibly:
- the losses are minimal
- the useful work obtained is maximal
- this work is very significant
- it is represented by the Gibbs free energy

\[ dG = -FEDN \] (18)
Maximum useful work
Substituting eqn. 18 in eqn. 17 we get:

\[ dG = dH - TdS \] (19)

This is the thermodynamic expression for the maximum useful work obtainable from a system.

Interpretation
\[ dG = dH - TdS \] (19)
From a practical viewpoint:
- \( H \) represents the total energy of the system
- \( S \) represents the “unavailable” energy – the unavoidable losses that cannot be circumvented
- \( G \) therefore represents the “free” energy – or the energy available to do useful work

Significance of \( G \)
- \( G \) - related to the \( H \) and the \( S \) (eqn. 19)
- Neither directly related to reaction in eqn. 6
- But the reaction does contribute to energy production – intuitive reasoning

Some property of the reactants and products defines their tendency to react, and influences the free energy - What is it?

The chemical potential (\( \mu \))
- Independent of mass and path
- Has a constant value at equilibrium for a given substance through all the phases in which it is present as a component
- A property that estimates tendency of substance to react
- A property that is related to \( G \)

Mathematical significance
\[ dU = dQ - dW \] (20)
- We write \( dQ \) as \( TdS \) (2nd law)
- We replace \( dW \) with the pressure volume term and a “useful work” term
- The useful work = \((\text{intensity factor } (\mu)) (\text{capacity factor } (n))\)

\[ dU = TdS - PdV + \sum \mu_i d\eta_i \] (21)
- Where the product between \( \mu_i \) and \( \eta_i \) represents useful work done by a single species
- The summation is done to include contribution of all species

- Introducing \( H \) instead of \( U \) and \( PV \), we have:

\[ dH = TdS + \sum \mu_i d\eta_i \] (22)

- Comparing with eqn. 19, we can state:

\[ dG = \sum \mu_i d\eta_i \] (23)

Relation between \( G \) and \( \mu \) - an intrinsic quantity that bears a relation to the reactants and products in equation 6.
More on $\mu$

- $\mu$ is an intensive property – mass independent
- Does not define the amount of species present
- This is obtained from gas pressure / concentrations

Direct link between $\mu$ and concentration - difficult to obtain
- Such a link – needed – developed using invented functions such as activity
- Note – activity = partial pressure for an ideal gas

Developing the link – ideal gases

\[ G = H - TS \] (24)

Therefore:
\[ dG = dH - TdS - SdT \] (25)

Now:
\[ H = U + PV \] and  \[ dH = dU + PdV + VdP. \]

Therefore:
\[ dG = dU + PdV + VdP - TdS - SdT \] (26)

We know:
\[ dU = TdS - PdV + \sum \mu_i d n_i \] (21)

Sub. Eqn. 21 in Eqn. 26,
\[ dG = TdS - PdV + \sum \mu_i d n_i + PdV + VdP - TdS - SdT \] (27)

Which simplifies to:
\[ dG = VdP - SdT + \sum \mu_i d n_i \] (28)

By partially differentiating equation (28) w.r.t. P:

\[ \left( \frac{\delta G}{\delta P} \right)_{T, n} = V \] (29)

For ideal gases:
\[ V = n \frac{RT}{P} \] (30) – ideal gas law
\[ n = \text{no. of moles} \]
And
\[ \left( \frac{\delta G}{\delta P} \right)_{T, n} = nRT / P \] (31)

Expression for $\Delta G$

Upon integration, eqn. 31 gives:

\[ \Delta G = G - G^* = nRT \ln \left( \frac{P}{P^*} \right) \] (32)

Since only differences in $G$ are significant from a practical viewpoint, a standard state is generally chosen, and is represented by the superscript $^*$. 
\[ \Delta G \text{ for a single species in solution} \]

Replacing the pressure for the component partial pressure in eqn. 31:

\[ \Delta G_i = G_i - G_i^o = n_iRT \ln \left( \frac{p_i}{p_i^o} \right) \quad (33) \]

Link between \( \Delta G \) and partial pressure (\( p \)) established. Now need link between \( \mu \) and \( p \)

\[ \Delta G \text{ for a reaction} \]

For a given reaction:

\[ \Delta G = \Sigma \nu_p \mu_p - \Sigma \nu_r \mu_r \quad (35) \]

Where:

\( \nu \) - stoichiometric number (coefficient of reactant and product species)

\( p, r \) - products and reactants respectively

Another statement of the first law of thermodynamics – energy is conserved

\[ \text{The significance of EMF (E)} \]

Also, eqn. 18 upon integration gives:

\[ \Delta G = -NFE \quad (36) \]

Thus,

\[ \Delta G = \Sigma \nu_p \mu_p - \Sigma \nu_r \mu_r = -NFE \]

This equation exemplifies the significance of the EMF as a measure of chemical potential

\[ \text{Case 1 – standard state} \]

All the gases (reactants and products) are at unit pressure

Therefore:

\[ \ln \{ \Pi (p_p^o/p_r^o) \} = 0 \]

Hence, eqn. 37 reduces to:

\[ \Delta G^o = \Sigma \nu_p \mu_p^o - \Sigma \nu_r \mu_r^o = -NFE^o \quad (38) \]

\[ \text{Some fancy math} \]

Substituting equation 34 into equation 35, and combining equations 35 and 36 we have:

\[ \Delta G = \Sigma \nu_p \mu_p^o - \Sigma \nu_r \mu_r^o + RT \ln \{ \Pi (p_p^o/p_r^o) \} = -NFE \quad (37) \]

This equation provides a link between tangible measures such as partial pressures and the EMF
Case 2 – equilibrium

$\Delta G = 0$

$\Pi(p_p^{\nu}/p_r^{\nu}) = K$ (equilibrium constant)

In this case, eqn 37 becomes:

$\Sigma\nu_p\mu_p^0 - \Sigma\nu_r\mu_r^0 + RT \ln K = 0 = -NEF$ (39)

Equilibrium relationship

Substituting equation 38 into equation 39:

$\Delta G^0 = -RT \ln K = -NFE^o$ (40)

This equation is valid only under equilibrium conditions, and relates the Gibbs free energy and the EMF to the equilibrium constant.

General relationship

Under non-equilibrium conditions:

$\Delta G = \Delta G^0 + RT \ln \Pi(p_p^{\nu}/p_r^{\nu}) = -NFE$ (41)

This is obtained by substituting eqn. 38 in eqn. 37.

This equation relates EMF with tangible quantities that define a given reaction.

Note that this is valid only for ideal gases. Similar (more complex) relationships can be obtained for real gases using the appropriate gas laws.

The Nernst equation

$\Delta G^0 + RT \ln \Pi(p_p^{\nu}/p_r^{\nu}) = -NFE$ (41)

dividing throughout by NF we get:

$\Delta G^0/ NF + (RT/ NF) \ln \Pi(p_p^{\nu}/p_r^{\nu}) = -E$ (42)

From eqn. 40:

$\Delta G^0/ NF = -E^o$

Therefore eqn. 42 becomes:

$-E^o + (RT/ NF) \ln \Pi(p_p^{\nu}/p_r^{\nu}) = -E$ (43)

Which on rearrangement gives:

$E = E^o - (RT/ NF) \ln \Pi(p_p^{\nu}/p_r^{\nu})$ (44)

Eqn. 44 is called the Nernst equation.

Significance of the Nernst equation

 Widely used in electrochemistry to evaluate the effect of simple changes in reactant or product activity, and temperature on the cell voltage.

For example:

A 10 fold increase in a reactant gas partial pressure at 298 K – 60 mV increase in E when N = 1
## The Carnot efficiency

Any heat engine that absorbs heat at a high temperature ($T_1$) must reject energy at a lower temperature ($T_2$) to do useful work.

The efficiency (Carnot efficiency) of an ideal engine - limited by the second law is given by:

\[ \eta_{\text{carnot}} = 1 - \frac{T_2}{T_1} \] (45)

### Interpretation

- Efficiency is 1 for an infinitely hot source.
- Higher the hot source temp., higher the efficiency.

Specious argument - the energy lost due to irreversible processes in maintaining the hot source temperature far exceeds the work output of the cell - thereby leading to reduced efficiencies.

The efficiency of a Carnot engine is quite low!

## Fuel cells vs. Carnot engines

- Fuel cells – isothermal operation – no temperature cycling.
- Less energy lost in maintaining the temperature of the “hot source”.
- Fuel cells - inherently less irreversible.

**Fuel cells - not limited by the Carnot efficiency**

## Fuel cell efficiency – 1st law

\[ \eta = \frac{W_{\text{out}}}{Q_{\text{in}}} \] (46)

- Work done ($W$) is given by the $\Delta G$ (or NFE).
- Heat input ($Q$) calculated based upon the higher heating value (HHV) of the fuel.

\[ \eta = \frac{\Delta G}{HHV} = \frac{\text{NFE}}{\text{HHV}} \] (47)

## Max efficiency – 1st law

The maximum efficiency occurs at standard conditions – highest possible cell voltage.

\[ \eta_{\text{max}} = \frac{\Delta G^o}{HHV} = \frac{\text{NFE}^o}{\text{HHV}} \] (48)

For a typical H2/O2 fuel cell, the maximum efficiency calculated from eqn. 48 is ~83%.

## How does a Carnot engine match up?

A Carnot engine would have to have a high temperature of 1753 K (with a corresponding low temperature of 298K) to achieve this efficiency (83%)!
Caution

- Work done by a Carnot cycle engine (and hence the Carnot efficiency) increases with increasing temperature (of the hot source)
- The reverse is true for the $\Delta G$ based fuel cell efficiency
- This is because $\Delta G$ (and hence $E$) decreases with temperature (Recall Nernst equation)

Fuel cell vs. Carnot efficiencies – Temperature dependence

- There therefore exists a temperature beyond which the fuel cell efficiency is actually lower than the Carnot efficiency – see previous fig.
- This temperature - approximately 950 K for a H2/O2 system

Moral

- Often reported in literature / presentations / proposals (quite erroneously):
  
  “A fuel cell is 100% efficient”

  NOT TRUE!

  Better stated as:

  “The fuel cell is not limited by the Carnot efficiency”

Limitation of 1st law efficiency

- Max efficiency from eqn. 48 – quite meaningless from a practical standpoint
- Reason? – no current drawn (open circuit conditions)

Practical efficiency – 2nd law

Indicates the actual work obtained to the maximum possible work obtainable

$$\eta_{2nd\ law} = \frac{NFE}{NFE^o} = \frac{E}{E^o} \ (49)$$

also referred to as a voltage efficiency
Other efficiencies – current efficiency

Ratio of the current produced to the current expected (based on Faraday’s law) for the amount of fuel fed to the cell

$$\eta_i = \frac{I}{NF \frac{dn}{dt}} \quad (50)$$

$n$ – no. of moles of fuel

This efficiency can indeed be close to 100% - is misleading as it does not refer to the efficiency with which work is done by the cell

Other efficiencies - Gibbs free energy efficiency

This is simply the product of the current and voltage efficiencies

Calculating ideal fuel cell voltage