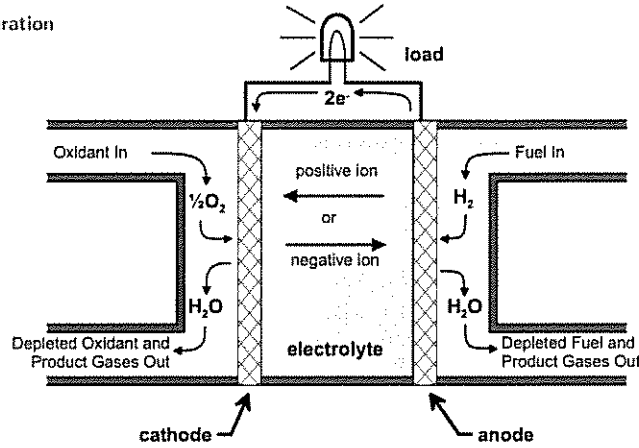


Fuel Cell Operation



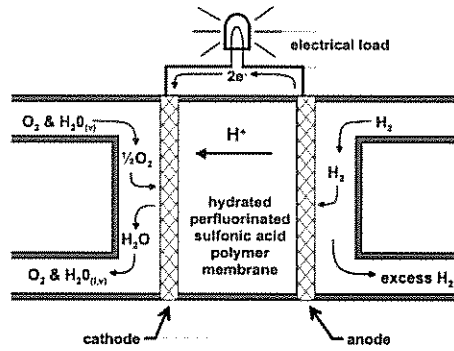
- electrochemical energy conversion device
- nonconsumable anode and cathode
- oxidation-reduction reaction converted directly into electrical energy without a intermediary conversion into heat – more efficient than the Carnot cycle – as high as 90% efficiency theoretically possible
- reactants (typically gaseous) external to energy conversion device
- electrolyte layer in contact with a porous anode and cathode, provides reactant and ionic transport as well as physical barrier to separate fuel and oxidant
- ionic transport can be positive or negative

Fuel Cell Classification

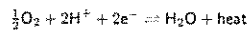
	PEMFC*	AFC	PAFC	MCFC	SOFC
electrolyte	ion exchange membrane	KOH in asbestos matrix	phosphoric acid in silicon carbide	alkali carbonates in LiAlO ₂ matrix	ceramics <i>yttria, zirconia</i>
charge carrier	H ⁺	OH ⁻	H ⁺	CO ₃ ²⁻	O ²⁻
operating temperature	~ 80°C	~ 100°C	~ 200°C ~ 220°C	~ 650°C	~ 1000°C
catalyst	platinum	various	platinum	nickel	perovskites
product water management	evaporative (hopefully)	<i>evaporative</i>	evaporative	gaseous product	gaseous product
product heat management	process gas & cooling system	<i>cooling system</i>	process gas & cooling system	internal reforming & process gas <i>co-generation</i>	internal reforming & process gas <i>co-generation</i>
fuel	pure H ₂ , tolerates CO ₂	pure H ₂ - no CO ₂	pure H ₂ tolerates CO ₂ ~ 1% CO	H ₂ , CO, CH ₄ , other hydrocarbons	H ₂ , CO, CH ₄ , other hydrocarbons

* Also known as solid polymer fuel cell (SPFC)

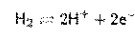
PEM Fuel Cell Kinetics



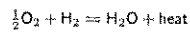
O₂ reduction half reaction - cathode



H₂ oxidation half reaction - anode

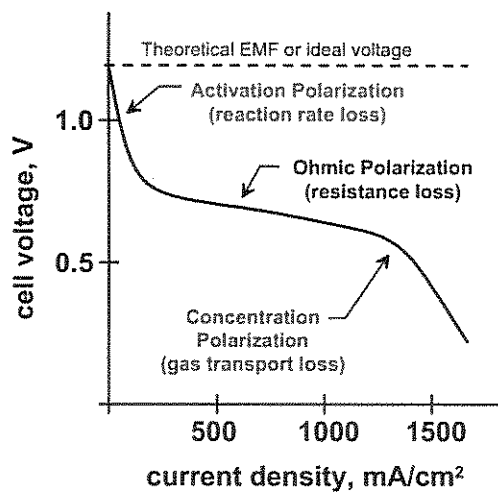


overall cell reaction



performance limited by rate of O₂ reduction which is more than 100 times slower than the H₂ oxidation

Polarization Losses



Activation Polarization losses due to oxidation/reduction kinetics

Ohmic Polarization losses due to resistance in electron and ionic conduction

Concentration Polarization excess water "floods" the gas diffusion layer or "plugs" the gas flow channel

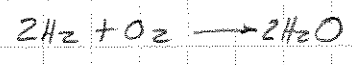
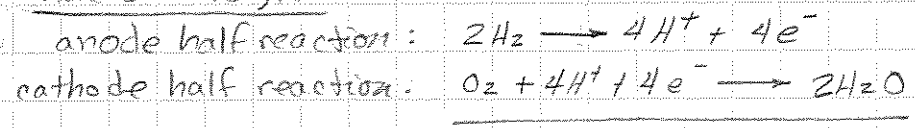
water management is critical to the performance of a PEM fuel cell

Electrochemical Reactions

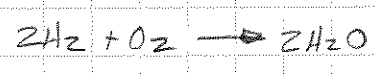
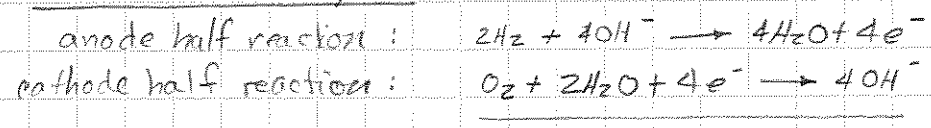
common fuels

- H₂
- CH₄
- C₃H₈
- CO
- C
- CH₃OH
- CH₂O₂
- NH₃
- N₂H₄

Acid Electrolyte



Alkaline Electrolyte

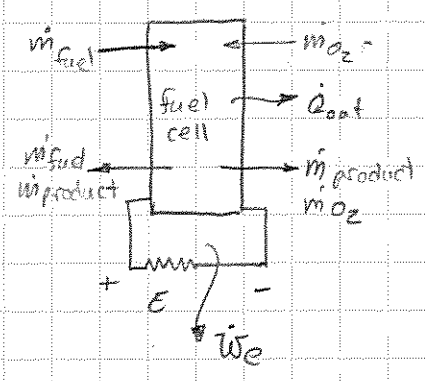


Energy Available for Conversion

The total energy change of the reactants is the difference in enthalpy of formation.

$$\Delta H_f = \sum_{\text{products}} \Delta H_f - \sum_{\text{reactants}} \Delta H_f$$

$\Delta H_f > 0$ exothermic
 $\Delta H_f < 0$ endothermic



Apply Cons. of Energy to the Control Volume

$$\dot{Q}_{out} - \dot{W}_e = \Delta \dot{E} = \Delta \dot{H} \quad \left\{ \begin{array}{l} \text{no changes in kinetic or} \\ \text{gravitational potential energies} \end{array} \right.$$

↑
total change in enthalpy

The maximum work (power) will occur if the thermal power portion of the enthalpy change is reversible.

$$\dot{Q}_{Rev} = T \dot{S}$$

Fuel cells typically operate isothermally, therefore,

$$\dot{Q}_{out} = T \dot{\Delta S}$$

$$-\dot{W}_e \leq \underbrace{\Delta \dot{H} - T \dot{\Delta S}}$$

↑ known as change in Gibbs Free Energy, $G = H - TS$

$$-\dot{W}_e \leq \sum_{\text{products}} \dot{G} - \sum_{\text{reactants}} \dot{G}$$

criteria for a spontaneous reaction:
 $dG_{T,p} = \delta Q - T \delta S \leq 0$

Gaseous Reactants

▣ Treating the reactants as an ideal gas, $PV = n\bar{R}T$
 n = # of mds

• for an ideal gas $Tds = dh - \bar{V}dP$ (Gibbs equation)

$$\hookrightarrow dG = dH - TdS = \bar{V}dP$$

$$\hookrightarrow dG = n\bar{R}T \frac{dP}{P}$$

• for an isothermal process

$$G_2 - G_1 = n\bar{R}T \ln\left(\frac{P_2}{P_1}\right)$$

▣ Tabulated values of Gibbs Free Energy (and enthalpy of formation) are given relative to a reference state.

$$G = G^\circ + n\bar{R}T \ln\left(\frac{P}{P^\circ}\right)$$

\hookrightarrow reference state; typically at $P^\circ = 1 \text{ atm}$ (BUT NOT ALWAYS!)

$\frac{P}{P^\circ}$ is also known as activity

Electrical Work

$$W_e = n_e F E$$

\uparrow voltage difference across electrodes
 \uparrow Faradays constant = $96487 \frac{\text{C}}{\text{mol e}^-}$
 \uparrow mds of electron per mol of fuel

The change in Gibbs Free Energy at reference state is $\Delta G^\circ = -n_e F E^\circ$

$$\text{Thus, } E^\circ = \frac{-\Delta G^\circ}{n_e F}$$

\nearrow open circuit potential (no current flow)

Maximum Conversion Efficiencies

$$\text{Heat Engine: } \eta_{th} = 1 - \frac{T_{low}}{T_{high}}$$

$$\text{Fuel Cell: } \eta_{th} = \frac{W_e}{HV} = \frac{\Delta G}{\Delta H} = \frac{n_e F E}{\Delta H}$$

$$\eta_{th, max} = \frac{n_e F E^\circ}{\Delta H}; \text{ For H}_2\text{-O}_2 \text{ reaction at } 25^\circ\text{C and } 1 \text{ atm, } E^\circ = 1.23 \text{ V.}$$

3.6.3. Thermodynamic Efficiency

For the case of an electrochemical energy converter working ideally, it has been shown that the free-energy change of the reaction may be totally converted to electrical energy. Thus, an electrochemical energy converter has a thermodynamic efficiency given by:

$$\eta_{th} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \quad (3.65)$$

Table 3-1. Thermodynamic Data for some Candidate Fuel-Cell Reactions Under Standard Conditions at 25 °C.

Fuel	Reaction	n	$-\Delta H^0$ [kJ/mol]	$-\Delta G^0$ [kJ/mol]	E^0 rev. [V]	%
Hydrogen	$H_2 + 0.5 O_2 \longrightarrow H_2O_{(l)}$	2	286.0	237.3	1.229	83.0
	$H_2 + Cl_2 \longrightarrow 2 HCl_{(aq)}$	2	335.5	262.5	1.359	78.3
	$H_2 + Br_2 \longrightarrow 2 HBr$	2	242.0	205.7	1.066	85.0
Methane	$CH_4 + 2 O_2 \longrightarrow CO_2 + 2 H_2O_{(l)}$	8	890.8	818.4	1.060	91.9
Propane	$C_3H_8 + 5 O_2 \longrightarrow 3 CO_2 + 4 H_2O_{(l)}$	20	2221.1	2109.9	1.093	95.0
Decane	$C_{10}H_{22} + 15.5 O_2 \longrightarrow 10 CO_2 + 11 H_2O_{(l)}$	66	6832.9	6590.5	1.102	96.5
Carbon monoxide	$CO + 1.5 O_2 \longrightarrow CO_2$	2	283.1	257.2	1.066	90.9
Carbon	$C + 0.5 O_2 \longrightarrow CO$	2	110.6	137.3	0.712	124.2
	$C + O_2 \longrightarrow CO_2$	4	393.7	394.6	1.020	100.2
Methanol	$CH_3OH + 1.5 O_2 \longrightarrow CO_2 + 2 H_2O_{(l)}$	6	726.6	702.5	1.214	96.7
Formaldehyde	$CH_2O_{(g)} + O_2 \longrightarrow CO_2 + 2 H_2O_{(l)}$	4	561.3	522.0	1.350	93.0
Formic acid	$HCOOH + 0.5 O_2 \longrightarrow CO_2 + H_2O_{(l)}$	2	270.3	285.5	1.480	105.6
Ammonia	$NH_3 + 0.75 O_2 \longrightarrow 0.5 N_2 + 1.5 H_2O$	3	382.8	338.2	1.170	88.4
Hydrazine	$N_2H_4 + O_2 \longrightarrow N_2 + 2 H_2O_{(l)}$	4	622.4	602.4	1.560	96.8

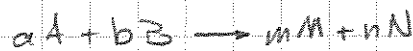
Finding ΔG

		heat of formation \bar{h}_f° [kJ/kmol]	Gibbs free energy \bar{g}° [kJ/kmol]
hydrogen gas	H ₂	0	0
oxygen gas	O ₂	0	0
water vapor	H ₂ O _(v)	-241820	-228570
liquid water	H ₂ O _(l)	-285830	-237180
carbon monoxide	CO	-110530	-137150
carbon dioxide	CO ₂	-393520	-393360

from Cengel & Boles, Table A-26

On a molar basis, $\bar{g} = \bar{g}^\circ - RT \ln(P/P_0)$; P_0 is the reference state pressure, which is typically 1 atm

- For a generic chemical reaction



where A is the fuel and a, b, c, and d are the stoichiometric conditions.

$$\Delta \bar{g} = \underbrace{(m\bar{g}_m - n\bar{g}_n)}_{\text{products}} - \underbrace{(a\bar{g}_A - b\bar{g}_B)}_{\text{reactants}}$$

- On a per mol of fuel basis,

$$\begin{aligned} \Delta \bar{g} &= \left(\frac{m}{a}\right)\bar{g}_m + \left(\frac{n}{a}\right)\bar{g}_n - \bar{g}_A - \left(\frac{b}{a}\right)\bar{g}_B \quad \left[\frac{\text{kJ}}{\text{kmol fuel (A)}}\right] \\ &= \left\{ \left(\frac{m}{a}\right)\bar{g}_m^\circ + \left(\frac{n}{a}\right)\bar{g}_n^\circ - \bar{g}_A^\circ - \left(\frac{b}{a}\right)\bar{g}_B^\circ \right\} - \left\{ \left(\frac{m}{a}\right)RT \ln\left(\frac{P_m}{P_0}\right) + \left(\frac{n}{a}\right)RT \ln\left(\frac{P_n}{P_0}\right) - \dots \right\} \end{aligned}$$

- collecting terms,

$$\Delta \bar{g} = \Delta \bar{g}^\circ - RT \ln \left\{ \frac{\left(\frac{P_m}{P_0}\right)^{m/a} \left(\frac{P_n}{P_0}\right)^{n/a}}{\left(\frac{P_A}{P_0}\right)^1 \left(\frac{P_B}{P_0}\right)^{b/a}} \right\}$$

known as the reaction coefficient, K

$$\Delta \bar{g} = \Delta \bar{g}^\circ - RT \ln K$$

- When the reference pressure is 1 atm, and reactant/product pressures are expressed in atm, and when the stoichiometric coefficient for the fuel is 1 mol ($a=1$), then the change in Gibbs free energy is commonly written as:

$$\Delta g = \Delta \bar{g}^\circ + RT \ln \left(\frac{P_A P_B^b}{P_m^m P_n^n} \right) \quad \leftarrow \text{Note the sign change.}$$

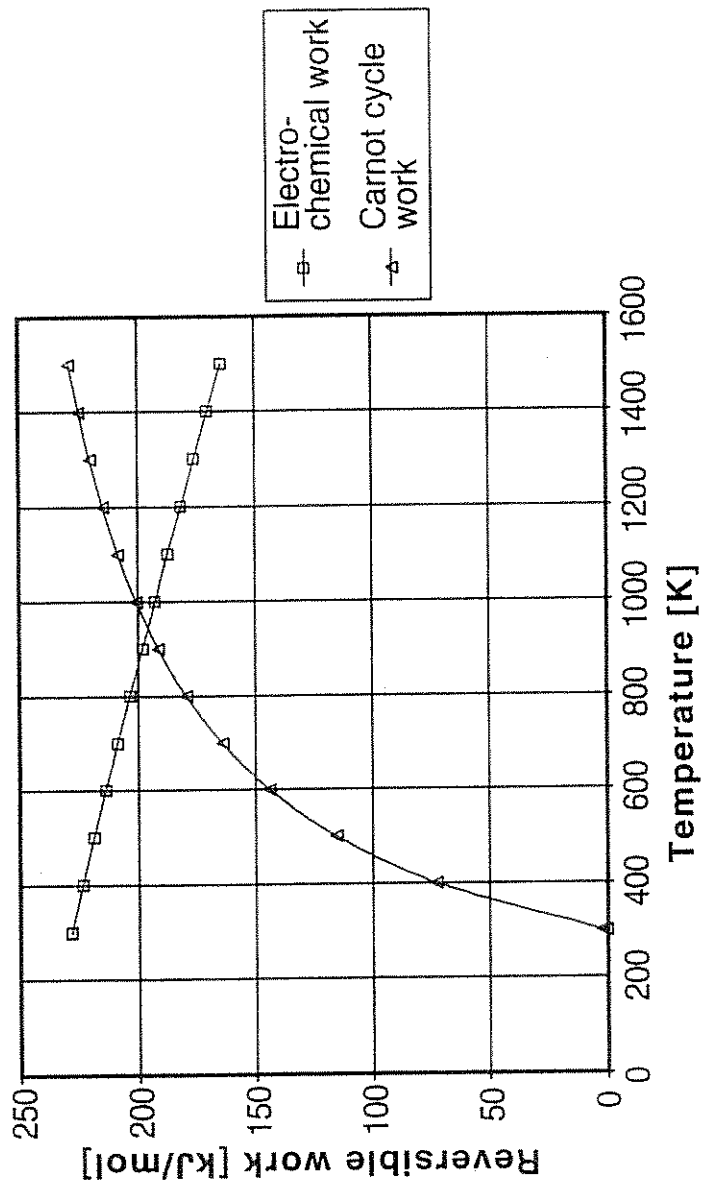
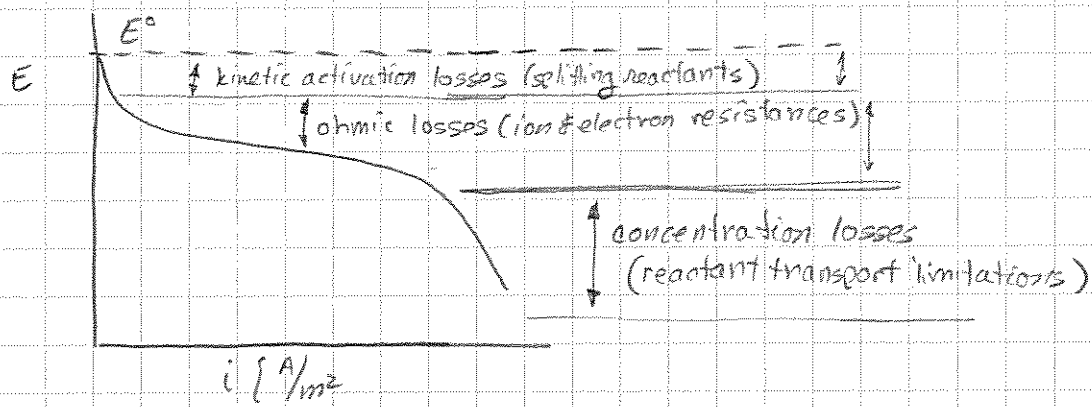


FIGURE 3.10 The reversible work produced by a H_2/O_2 fuel cell is greater than that of a Carnot engine at temperatures below 950 K. At higher temperatures, the Carnot engine is able to convert more of the *HHV* of H_2 (285.840 kJ/mol) into work. The data for the standard Gibbs energy of formation for water vapor was taken from Lide (1995, pp. 5–64).

Polarization Curve



At non-standard states,

$$E = E^{\circ} + \frac{RT}{n_e F} \ln \left[\frac{\sum \left(\frac{\text{Reactants}}{P_0} \right)^m}{\sum \left(\frac{\text{Products}}{P_0} \right)^n} \right] \quad \text{Nernst Equation}$$

H₂ heating value at 300°C

Determine the heating value of H₂ at 300°C. Reactants and oxidants are at 1 atm.



at 300°C & 1.1 atm, this will be in vapor form.

$$\Delta \bar{h}^\circ = \underbrace{\sum n_p \bar{h}_f^\circ}_{\text{products}} - \underbrace{\sum n_r \bar{h}_f^\circ}_{\text{reactants}}$$

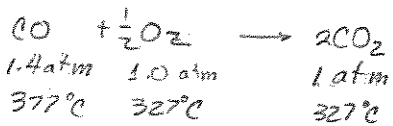
$$\Delta \bar{h}^\circ = \left[\left(1 \frac{\text{kmol H}_2\text{O}}{\text{kmol H}_2} \right) \left(-285830 \frac{\text{kJ}}{\text{kmol H}_2\text{O}} \right) \right] - \left[\left(1 \frac{\text{kmol H}_2}{\text{kmol H}_2} \right) (0) + \left(\frac{1}{2} \frac{\text{kmol O}_2}{\text{kmol H}_2} \right) (0) \right]$$

$$\Delta \bar{h}^\circ = -285830 \frac{\text{kJ}}{\text{kmol H}_2\text{O}} = -\overline{\text{HHV}}_{\text{H}_2} = -(\overline{\text{LHV}} + \bar{h}_{fg})$$

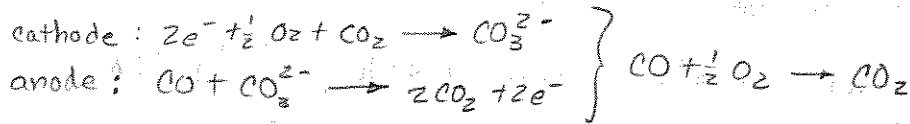
$\left. \begin{array}{l} \text{liquid water} \\ \text{product} \end{array} \right\}$ $\left. \begin{array}{l} \text{vapor} \\ \text{product} \end{array} \right\}$ $\left. \begin{array}{l} \text{enthalpy of} \\ \text{vaporization} \end{array} \right\}$

$$\Delta \bar{h}_{(v)}^\circ = \Delta \bar{h}_{(l)}^\circ - \bar{h}_{fg}(300^\circ\text{C}) = -241820 \frac{\text{kJ}}{\text{kmol H}_2}$$

CO Fuel Cell @ 327°C



Determine the cell voltage and efficiency for CO reacting in air.



$$E = E^\circ - \frac{RT}{neF} \ln \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}} P_{\text{O}_2}^{1/2}} \right) \quad ; P_0 = 1 \text{ atm}$$

$$E^\circ = \frac{\Delta \bar{g}^\circ}{neF}$$

$$\Delta \bar{g}^\circ = 1 \bar{g}^\circ_{\text{CO}_2} - \bar{g}^\circ_{\text{CO}} - 0.5 \bar{g}^\circ_{\text{O}_2} = \left(-394360 \frac{\text{kJ}}{\text{kmol}} \right) - \left(-137150 \frac{\text{kJ}}{\text{kmol}} \right) - \frac{1}{2}(0)$$

$$E^\circ = - \frac{\left(-257210 \frac{\text{kJ}}{\text{kmol CO}} \right)}{\left(2 \frac{\text{kmol } e^-}{\text{kmol CO}} \right) \left(96489 \frac{\text{C}}{\text{kmol } e^-} \right)} = 1.33 \text{ V} \quad \left(\text{open circuit potential at reference state} \right)$$

$$E = E^\circ - \frac{RT}{neF} \ln \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}} P_{\text{O}_2}^{1/2}} \right) = 1.33 \text{ V} - \frac{\left(8.134 \frac{\text{kJ}}{\text{kmol } \cdot \text{K}} \right) (600 \text{ K})}{\left(2 \frac{\text{kmol } e^-}{\text{kmol CO}} \right) \left(96489 \frac{\text{C}}{\text{kmol } e^-} \right)} \ln \left(\frac{1}{1.4 (1.0 \times 0.21)^{0.5}} \right)$$

↑ fraction of O₂ in air

$$= 1.33 \text{ V} - (0.0253 \text{ V})(0.4433)$$

$$E = 1.319 \text{ V} \quad \left(\text{open circuit potential at } 327^\circ\text{C} \text{ \& } P_{\text{CO}} = 1.4 \text{ atm} \right)$$

$$\Delta \bar{g} = -neFE = -254494 \frac{\text{kJ}}{\text{kmol CO}}$$

$$\Delta \bar{h}^\circ = -282990 \frac{\text{kJ}}{\text{kmol CO}}$$

$$\left. \begin{array}{l} \Delta \bar{g} = -254494 \frac{\text{kJ}}{\text{kmol CO}} \\ \Delta \bar{h}^\circ = -282990 \frac{\text{kJ}}{\text{kmol CO}} \end{array} \right\} \eta_{\text{max}} = \frac{\Delta \bar{g}}{\Delta \bar{h}^\circ} = 0.8993$$