

## Chapter 9

### Fuel Cells

#### Problem Solutions



**Prob 9.1** Every substance is endowed with a certain amount of energy and a certain amount of entropy. While the latter is well defined, the former—the energy—has no absolute value; only changes in energy can be measured. For this reason (entirely by convention), the enthalpy of formation of elements in their natural state is taken as zero.

Consider aluminum and oxygen. In their natural states, their standard enthalpy of formation (i.e., the energy of formation at STP) is, as we said, zero. Every kilogram of aluminum has (at STP) an entropy of 1.05 kJ/K, whereas every kilogram of oxygen has an entropy of 6.41 kJ/K.

Aluminum burns fiercely forming an oxide ( $\text{Al}_2\text{O}_3$ ) and releasing energy. The standard enthalpy of formation of the oxide is -1.67 GJ/kmole. The entropy of the oxide is 51.0 kJ/K per kilomole.

According to the second law of thermodynamics, the entropy of a closed system suffering any transformation can not diminish. It can, at best, remain unchanged as the result of the transformation or else, it must increase. If you add up the entropies of the aluminum and of the oxygen, you will discover that the sum exceeds the entropy of the oxide formed. This means that when aluminum combines with oxygen, only part of the chemical energy can be transformed into electricity, while the rest must appear as the heat associated with the missing entropy. That part that can (ideally) be converted into electricity is called the free energy.

Calculate the free energy of the aluminum/oxygen reaction.

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Here are the data required:

MATERIAL	ENTROPY	STANDARD ENTHALPY OF FORM.	MOLECULAR MASS
	kJ/K	GJ/K per kmole	daltons
Aluminum	1.05 per kg	0	26.98
Oxygen	6.41 per kg	0	32.00
$\text{Al}_2\text{O}_3$	51.0 per kmole	-1.67	

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Remember that we defined RTP (reference temperature and pressure) as a pressure of 1 atmosphere and a temperature of 298.15 K. This differs from the usual STP (standard temperature and pressure) which is defined as a pressure of 1 atmosphere and a temperature of 273.15 K.

## Solution of Problem 9.1

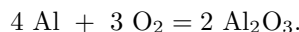
Most of the data above are given in the problem statement, but we have to look up the molecular masses of the materials under discussion. At least, we have to look up the atomic mass of aluminum. We may remember that the dalton is defined as  $1/32$  of the molecular mass of  $O_2$ , so that the mass of the latter is exactly 32.00 daltons. Once we know the masses of Al and  $O_2$ , we can easily calculate that of  $Al_2O_3$ .

The free energy is

$$\Delta G = \Delta H - T\Delta S$$

where  $T\Delta S$  is the heat that must appear to compensate the change in entropy owing to the reaction.

The reaction involved in the formation of aluminum oxide from its elements is



At RTP, the entropy of aluminum is  $1.05 \text{ kJ K}^{-1}\text{kg}^{-1}$ , as given in the problem statement. Since the atomic mass of Al is 27.0, the entropy is  $1.05 \times 27 = 28.4 \text{ kJ K}^{-1}\text{kmole}^{-1}$ .

In a similar manner, the entropy of  $O_2$  was given as  $6.41 \text{ kJ K}^{-1}\text{kg}^{-1}$  or  $6.41 \times 32 = 205.1 \text{ kJ K}^{-1}\text{kmole}^{-1}$ .

Consequently, the entropy of the reactants is  $4 \times 28.4 + 3 \times 205.1 = 729.0 \text{ kJ K}^{-1}$ . On the other side of the equation, the entropy of the products is  $2 \times 51.0 = 102 \text{ kJ K}^{-1}$ .

Considering only the matter balance, the reaction causes an entropy reduction of  $729.0 - 102.0 = 627 \text{ kJ K}^{-1}$  or  $627.0/2 = 313.5 \text{ kJ K}^{-1}\text{kmole}^{-1}$  (of aluminum oxide). This contradicts the second law of thermodynamics, and a certain amount,  $Q$ , of heat must evolve.

Assuming that the reaction proceeds isothermally (heat is removed as fast as it is created), then  $Q = T\Delta S = 298 \times 313,500 = 93.4 \times 10^6$  joules per kilomole of oxide or 93.4 MJ per kilomole of oxide.

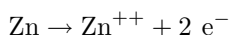
The enthalpy change owing to the reaction is 1670 MJ per kilomole of oxide. Of this,  $1670 - 93 = 1577$  is free energy and can (theoretically) be transformed into electricity.

The standard free energy of aluminum oxide is -1.577 GJ per kmole.

## Solution of Problem 9.1

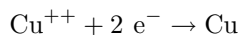
**Prob 9.2** Daniel cells used to be popular last century as a source of electricity, especially in telegraph systems. These cells consisted of a container divided into two compartments by a membrane permeable to ions. In one compartment, a zinc electrode was dipped in a zinc sulfate solution and, in the other, a copper electrode in a copper sulfate solution.

The zinc oxidizes (i.e., loses electrons):



The zinc is eroded, going into the solution in the form of ions.

At the other electrode, the copper is reduced (i.e., the copper ions in the sulfate accept electrons and the copper from the sulfate plates out onto the copper electrode):



The cell will deliver current until it runs out of either zinc or sulfate, whichever is less.

Assume the cell has 95 g of zinc and 450 ml of a 0.1 M  $\text{CuSO}_4$  solution. M stands for molarity: moles of solute per liter of solution. How long can this cell deliver a current of 2 A to a load?

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A 2 ampere current corresponds to the flow of 2 coulombs every second or  $2/1.6 \times 10^{-19} = 1.25 \times 10^{19}$  electrons per second. This is  $1.25 \times 10^{19}/6.02 \times 10^{26} = 2.08 \times 10^{-8}$  kmoles of electrons per second.

Since, in the reaction of interest, 1 kmole of zinc or 1 kmole of copper sulfate corresponds to 2 kmoles of electrons, the consumption of each of these “fuels” is  $1.04 \times 10^{-8}$  kmoles per second.

The atomic masses involved (in daltons) are

Zn	65.4
Cu	63.5
S	32.0
O	16.0
$\text{CuSO}_4$	$63.5 + 32 + 4 \times 16 = 159.5$

The zinc consumption rate is  $1.04 \times 10^{-8} \times 65.4 = 6.8 \times 10^{-7}$  kg/s. 0.095 kg of zinc will last  $0.095/6.8 \times 10^{-7} = 140,000$  s or 38.8 h.

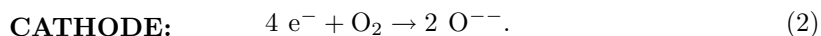
The  $\text{CuSO}_4$  consumption rate is  $1.04 \times 10^{-8} \times 159.5 = 1.66 \times 10^{-6}$  kg/s. We have 450 ml of 0.1 M solution of this salt. This solution contains  $0.1 \times 159.5$  kg of copper sulfate per cubic meter of water. Hence, our 450 ml contain 0.00718 kg of the salt. At the indicated consumption rate, this will last  $0.00718/1.66 \times 10^{-6} = 4325$  s or 72.1 min.

The cell will run out of copper sulfate much before it runs out of zinc. A “fuel cell” could be made by feeding in additional copper sulfate solution.

The limiting substance in the cell is copper sulfate which will run out in 72.1 minutes.

## Solution of Problem 9.2

**Prob 9.3** A fuel cell has the following reactions:



At RTP, the changes of enthalpy and of free energy, per kilomole of  $\text{CO}_2$ , are:

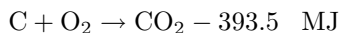
$$\Delta \bar{h}_f^\circ = -393.5 \text{ MJ},$$

$$\Delta \bar{g}_f^\circ = -394.5 \text{ MJ}.$$

What is the overall reaction? What is the ideal emf (i.e.,  $V_{rev}$ )? What is the difference in entropy between reactants and products?

Assume that the internal resistance of the cell is 1 milliohm. Otherwise, the cell behaves as an ideal voltage source. How much carbon is needed to deliver 1 MWh of electricity to the load in minimum possible time? What is the load resistance under such conditions?

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The overall reaction is



Since for each kilomole of product  $\text{CO}_2$ , 4 kilomoles of electrons circulate in the load ( $n_e = 4$ ), the open-circuit voltage is

$$|V_{oc}| = \frac{\Delta G}{(n_e q N_0)} = \frac{394.4 \times 10^6}{4 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 1.024 \text{ V}.$$

Assume that the cell operates isothermally at 298 K (reactants and products at the same temperature). Then,

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{(-393.5 + 394.5) \times 10^6}{298} = 3.36 \text{ kJ K}^{-1} \text{ kmole}^{-1}.$$

The above is, of course, per kilomole of  $\text{CO}_2$ .

Notice that in this reaction, owing to the free energy change being (in absolute value) larger than the enthalpy change, there is an *increase* in entropy. If the cell is to operate reversibly, i.e., with no entropy change, then it has to *absorb* heat—it will have to operate endothermically.

Let  $N$  be the number of kilomoles of carbon consumed. The electric energy generated will be  $W_e = |\Delta G|N$ , while the energy lost in the cell (owing to its internal resistance) will be  $I^2 R t$ , where  $t$  is the duration of the discharge (we assume constant current throughout the discharge).

The total charge that flows through the load is  $4NN_0 \times 1.6 \times 10^{-19}$  coulombs and the current is  $4NN_0 \times 1.6 \times 10^{-19}/t$  amperes.

## Solution of Problem 9.3

The energy,  $W_L$ , delivered to the load is the generated energy minus the internal losses:

$$W_L = |\Delta G|N - (4NN_0 \times 1.6 \times 10^{-19}/t)^2 R t = 1 \text{ MWh} = 3.6 \times 10^9 \text{ J.}$$

Introducing the values of  $\Delta G$ ,  $N_0$ , and  $R$ ,

$$3.94 \times 10^8 N - 1.49 \times 10^{14} N^2/t = 3.6 \times 10^9.$$

From this,

$$t = 3.76 \times 10^5 N^2/(N - 9.14),$$

$$\frac{dt}{dN} = 3.76 \times 10^5 \left[ \frac{2N}{(N - 9.14)} - \left( \frac{N}{N - 9.14} \right)^2 \right] = 0,$$

$$N = 18.3 \text{ kmols,}$$

$$t = 13.7 \times 10^6 \text{ seconds or 159 days.}$$

The current during the discharge is

$$\frac{4NN_0 \times 1.6 \times 10^{-19}}{t} = \frac{4 \times 18.3 \times 6.02 \times 10^{26} \times 1.6 \times 10^{-19}}{13.7 \times 10^6} = 515 \text{ A.}$$

The internal resistance of the cell is  $R = 0.001 \Omega$ , and the total resistance is  $R_L + R$ . The current delivered is, as we saw, 515 A, therefore,

$$R + R_L = \frac{V_{oc}}{I} = \frac{1.024}{515} = 0.002 \Omega,$$

$$R_L = 0.001 \Omega.$$

The overall reaction is  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ -393.5 MJ.

The ideal open-circuit voltage is 1.024 V.

The entropy change owing to the material balance in the reaction is  $+3.02 \text{ kJ K}^{-1} (\text{kmole of CO}_2)^{-1}$ .

To deliver 1 MWh, 18.3 kilomoles of carbon are needed.

The load resistance must be 1 milliohm.

## Solution of Problem 9.3

See a simpler solution below!

To transfer 1 MWh ( $3.6 \times 10^9$  J) in minimum time, means using maximum power. This is accomplished when  $R_L = R = 0.001 \Omega$ . The current that does this is

$$I_L = \frac{V_L}{R + R_L} = \frac{1.024}{0.002} = 512 \quad \text{A.}$$

The load voltage is

$$V_L = I_L R_L = 512 \times 0.001 = 0.512 \quad \text{V.}$$

The power in the load is

$$P_L = V_L I_L = 0.512 \times 512 = 262.1 \quad \text{W.}$$

The time necessary to deliver  $3.6 \times 10^9$  J at the rate of 262.1 J/s is

$$t = \frac{3.6 \times 10^9}{262.1} = 13.7 \times 10^6 \quad \text{s.}$$

The energy that the fuel cell must deliver is  $2 \times 3.6 \times 10^9 = 7.2 \times 10^9$  J because the internal loss is equal to the power in the load.

1 kilomole of carbon delivers 394.5 MJ of electricity. Thus, to deliver  $7.2 \times 10^9$  J, the number of kilomoles of carbon must be

$$N = \frac{7.2 \times 10^9}{394.5 \times 10^6} = 18.25 \quad \text{kmoles.}$$

These are the same results as before.

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## Solution of Problem 9.3



**Prob 9.4** The enthalpies and the free energies of formation (at RTP) of each species of interest in this problem are:

	$\Delta \bar{h}_f^\circ$ (MJ/kmole)	$\Delta \bar{g}_f^\circ$
CH <sub>3</sub> OH (g)	−201.2	−161.9
CH <sub>3</sub> OH (l)	−238.6	−166.2
O <sub>2</sub> (g)	0	0
CO <sub>2</sub> (g)	−393.5	−394.4
H <sub>2</sub> O (g)	−241.8	−228.6
H <sub>2</sub> O (l)	−285.9	−237.2

Owing to the methanol/oxygen reaction, reaction, the changes in enthalpy and in free energy are:

Methanol	Water	$\Delta \bar{h}^\circ$ MJ/kmole	$\Delta \bar{g}^\circ$ MJ/kmole
liquid	gas	−638.5	−685.3
gas	gas	−676.5	−689.6
liquid	liquid	−726.5	−702.4
gas	liquid	−764.5	−706.7

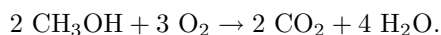
The values are per kilomole of methanol. Data from Dohle et al.

Consider methanol, a fuel that has been proposed for both internal combustion (IC) engines and for fuel cells. Methanol can be derived from fossil fuels and also from biomass. Being liquid at RTP conditions, it is a convenient fuel for automobiles. It has reasonable reactivity in fuel cells.

In IC engines, methanol is first evaporated and then burned. The engine exhausts water vapor. In fuel cells, the methanol reacts in liquid form but the product water is in vapor form.

**a. How much heat do you get by burning 1 kg of methanol in an IC engine?**

As with any hydrocarbon or alcohol, the combustion of methanol leads to the formation of carbon dioxide and water:



Both the methanol and the product water are in gaseous form. The heat of combustion is −676.5 MJ/kmole of methanol or −676.5/32 = 21.1 MJ per kg of methanol (molecular mass of methanol is 32 daltons). Liquid methanol would produce 20.0 MJ per kg. The difference is the heat of vaporization of the alcohol. This heat is absorbed by the carburetor from the environment. Notice that these are “lower” heats of combustion, i.e., heats of combustion corresponding to water vapor as a product.

In an IC engine, 1 kg of methanol yields 21.1 MJ of heat.

## Solution of Problem 9.4

**b. How much electric energy will an ideal fuel cell (using methanol and air) produce per kg of fuel?**

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Ideally, the electric energy generated by a fuel cell is equal to the free energy change owing to the reaction:

$$W_e = \frac{-\Delta G}{32} \quad \text{J/kg (methanol)}$$

The water is produced by the fuel cell in in vapor form. Thus, the  $\Delta G$  of the reaction would be -685.3MJ/kmole if the oxygen were at RTP. But the problem requires air as the oxidant, a gas in which the oxygen pressure is only 0.2 atm. The remaining fluids are still at 1 atmosphere. The free energy of each kilomole of oxygen is decreased (in absolute value) by an amount  $RT \ln 0.2 = 4.0$  MJ. Since there is 1.5 kilomoles of oxygen for each kilomole of methanol, the free energy of the reaction is now

$$\Delta G = -685.3 + 1.5 \times 4.0 = -679.3 \quad \text{MJ/kmole} \quad \text{or} \quad 21.2 \quad \text{MJ/kg.}$$

In an ideal fuel cell, 1 kg of methanol yields 21.2 MJ of electricity.

**c. How much heat does the cell reject?**

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The amount of heat an ideal fuel cell *absorbs* is

$$W_{heat} = |\Delta H| - |\Delta G| = 638.5 - 679.3 = 40.9 \quad \text{MJ/kmole}$$

or

$$1.28 \quad \text{MJ/kg of methanol.}$$

Notice that this ideal fuel cell operates endothermically, i.e., it absorbs heat from the environment, instead of rejecting it.

The cell absorbs 1.28 MJ of heat per kmole of methanol used.

**d. A practical OTTO cycle engine has an efficiency of, say, 20%, while a practical methanol fuel cell may have an efficiency of 60% (this is the efficiency of the practical cell compared with that of the ideal cell). If a methanol fueled IC car has a highway performance of 10 km per liter, what is the performance of the fuel cell car assuming that all the other characteristics of the cars are identical?**

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The energy delivered by a practical IC car per kilogram of methanol burned is

$$W_{IC} = 0.2 \times 21.1 = 4.2 \quad \text{MJ/kg,}$$

## Solution of Problem 9.4

while the energy delivered by a practical fuel-cell is

$$W_{FC} = 0.6 \times 21.2 = 12.7 \quad \text{MJ/kg.}$$

It follows that the highway performance of the fuel-cell car will be

$$\frac{12.7}{4.2} \times 10 = 30.3 \quad \text{km/liter.}$$

The fuel cell car has a kilometrage of 30.3 km/liter.

- e. If you drive 2000 km per month and a gallon of methanol costs \$2.40, how much do you save in fuel per year when you use the fuel cell version compared with the IC version? Can you think of other savings besides that in fuel?**

To drive  $12 \times 2000 = 24,000$  km per year, the fuel used will be:

For the IC car:  $24,000/10 = 2400$  liters.

For the FC car:  $24,000/30.3 = 792$  liters.

The fuel related annual savings of the FC car relative to the IC car is

$$(2400 - 792) \times \frac{\$2.4}{\text{gallon}} \times \frac{\text{gallon}}{3.78 \text{ liter}} = \$1020/\text{year.}$$

Yearly fuel savings are a modest \$1020/year

There would be some additional savings:

1. The FC car uses no oil.
2. The city mileage would be much closer to the highway mileage because of the simplicity of using regenerative braking in which the energy for decelerating the car is returned to the battery<sup>†</sup>
3. At a stop sign, the IC car consumes fuel while idling. The FC car consumes no energy when stopped.
4. The FC car requires no smog inspection, You save the cost of inspection.

- f. Suppose you get a ten year loan such that the yearly repayments of principal plus interest are 18% of the initial amount borrowed. By how much can the initial cost of the fuel-cell car exceed that of the IC car for you to break even? Assume that after 10 years the car is totally depreciated.**

Let  $P_{IC}$  and  $P_{FC}$  be, respectively, the price of the IC and that of the FC car.

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<sup>†</sup> The FC car would probably have a small battery for braking and fast acceleration.

## Solution of Problem 9.4

The car cost consists of the investment cost plus the fuel cost (neglecting maintenance, license and insurance).

Cost of the IC car:

$$0.18P_{IC} + \frac{2400 \times 2.4}{3.78} = 0.18P_{IC} + 1524 \quad \text{dollars per year.}$$

Cost of the FC car:

$$0.18P_{FC} + \frac{792 \times 1.2}{3.78} = 0.18P_{FC} + 502 \quad \text{dollars per year.}$$

We want

$$0.18P_{IC} + 1524 = 0.18P_{FC} + 502,$$

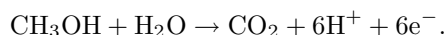
from which

$$P_{FC} = P_{IC} + 11,250.$$

We can afford to pay \$11,250 more for the FC car.

**g. What is the open circuit voltage of an ideal methanol fuel cell at RTP?**

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 From the anode reaction of the direct methanol fuel cell (see Section 9.4.5 of the Text), one can see that for each kilomole of methanol, 6 kilomoles of electrons are liberated, i.e,  $n_e = 6$ :



The relationship between the free energy change of a reaction and the open circuit voltage of an ideal fuel cell is

$$|\Delta G| = qn_e N_0 V,$$

$$V = \frac{|\Delta G|}{qn_e N_0} = \frac{|-679.3 \times 10^6|}{1.6 \times 10^{-19} \times 6 \times 6.02 \times 10^{26}} = 1.175 \quad \text{V.}$$

The ideal methanol fuel cell delivers 1.175 V when air is used.

## Solution of Problem 9.4

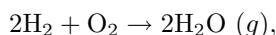
**Prob 9.5** An inventor wants to build a hydrogen manometer based on the dependence of the output voltage of a fuel cell on the pressure of the reactants. Take a  $\text{H}_2/\text{O}_2$  fuel cell operating at 298 K. Assume that it produces water vapor and that the open circuit voltage is that of an ideal cell. The oxygen pressure is maintained at a constant 0.1 MPa while the hydrogen pressure,  $p_{\text{H}_2}$ , is the quantity to be measured.

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**a. What is the output voltage when  $p_{\text{H}_2}$  is 0.1 MPa?**

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For the reaction



the free energy change is  $-228.6$  MJ/kmole of  $\text{H}_2\text{O}$  at RTP. Since for each kilomole of  $\text{H}_2\text{O}$ , 2 kilomoles of electrons are involved, the reversible voltage of the fuel cell is

$$V = \frac{|\Delta G|}{n_e q N_0} = \frac{228.6 \times 10^6}{1.6 \times 10^{-19} \times 2 \times 6.02 \times 10^{26}} = 1.185 \quad \text{V.}$$

The output voltage at 0.1 MPa is 1.185 V.

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**b. What is the output voltage when  $p_{\text{H}_2}$  is 1 MPa?**

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The pressure of the oxygen is unchanged but the hydrogen pressure is increased and the energy necessary to increase this pressure isothermally is free energy and will appear in the electric output of the cell. The energy is

$$W_{\text{press}} = RT \ln \frac{p_{\text{H}_2}}{p_{\text{H}_{20}}} = 8314 \times 298 \times \ln \frac{10^6}{10^5} = 5.70 \times 10^6 \quad \text{J/kmole of water.}$$

The free energy change of the reaction is increased (in absolute value) by the above amount.

$$|\Delta G| = |\Delta G_0| + 5.70 \times 10^6 = 234.3 \times 10^6 \quad \text{J/kmole of water.}$$

$$V = \frac{234.3 \times 10^6}{1.6 \times 10^{-19} \times 2 \times 6.02 \times 10^{26}} = 1.214 \quad \text{V.}$$

When the hydrogen pressure is raised to 1 MPa, the reversible voltage rises to 1.214 V. Notice that the voltage is not very sensitive to pressure.

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**c. Develop an expression showing the rate of change of voltage with  $p_{\text{H}_2}$ . What is this rate of change when  $p_{\text{H}_2}$  is 0.1 MPa?**

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$$V = \frac{|\Delta G|}{n_e q N_0}$$

**Solution of Problem 9.5**

$$\begin{aligned}
 \frac{dV}{dp_{H_2}} &= \frac{1}{n_e q N_0} \frac{d}{dp} |\Delta G| = \frac{1}{n_e q N_0} \frac{d}{dp} \left[ |\Delta G_0| + RT_0 \ln \left( \frac{p_{H_2}}{p_{H_{20}}} \right) \right] \\
 &= \frac{RT_0}{n_e q N_0} \frac{d}{dp} \left[ \ln \left( \frac{p_{H_2}}{p_{H_{20}}} \right) \right] = \frac{RT_0}{n_e q N_0 p_{H_2}} \\
 &= \frac{8314 \times 298}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26} p_{H_2}} = \frac{0.0128}{p_{H_2}} \quad \text{V/Pa.}
 \end{aligned}$$

At  $p_{H_2} = 0.1 \text{ MPa}$ ,

$$\frac{dV}{dp_{H_2}} = \frac{0.0128}{10^5} = 1.28 \times 10^{-7} \quad \text{V/Pa.}$$

At 0.1 MPa, the rate of change of voltage with pressure is a minute 0.128 microvolts per pascal.

- d. The output voltage of the cell is sensitive to temperature. Assume that a  $\pm 10\%$  uncertainty in pressure measurement can be tolerated (when the pressure is around 1 MPa). In other words, assume that when a voltage corresponding to 1 MPa and 298 K is read, the actual pressure is 0.9 MPa because the temperature of the gases is no longer 298 K. What is the maximum tolerable temperature variation?

From the Gibbs-Helmholtz equation:

$$\begin{aligned}
 \frac{dV}{dT} &\approx \frac{V - \frac{\Delta H}{n_e q N_0}}{T} = \frac{1.214 - \frac{241.8 \times 10^6}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}}}{298} \\
 &= \frac{1.214 - 1.255}{298} = -138 \times 10^{-6} \quad \text{V/K.}
 \end{aligned}$$

The problem requires that the change in voltage,  $\Delta V$  owing to the pressure error,  $\Delta p$ , be equal to the change in voltage owing to the temperature error.

$$\frac{dV}{dp} \Delta p = \frac{dV}{dT} \Delta T$$

or

$$\Delta T = \frac{dV/dp}{dV/dT} \Delta p = \frac{1.28 \times 10^{-8}}{138 \times 10^{-6}} \Delta p = 92.6 \times 10^{-6} \Delta p.$$

We note that the value of  $dV/dp$  at 1 MPa is  $1.28 \times 10^{-8} \text{ V/Pa}$ .

To keep the pressure reading error within 10% ( $10 \times 10^5$  at 1 MPa), the temperature must be kept within  $\pm 9.3 \text{ K}$ .

The temperature of the device must be kept within 9 C of 298 K.

The proposed manometer is not a good idea—large changes in pressure cause only very small changes in the observed voltage.

## Solution of Problem 9.5

**Prob 9.6** A certain gas, at  $10^5$  Pa, has a specific heat given by the expression  $c_p = a + bT + cT^2$  for  $298 \text{ K} < T < 2000 \text{ K}$ .

$$\begin{aligned} a &= 27.7 \text{ kJ K}^{-1} \text{ kmole}^{-1}, \\ b &= 0.8 \times 10^{-3} \text{ kJ K}^{-2} \text{ kmole}^{-1}, \\ c &= 10^{-6} \text{ kJ K}^{-3} \text{ kmole}^{-1}. \end{aligned}$$

The enthalpy of the gas is 0 at 298.0 K and its entropy, at this temperature, is  $130.0 \text{ kJ K}^{-1} \text{ kmole}^{-1}$ .

What are  $H$ ,  $G$  and  $S$  of the gas (per kilomole) at  $T = 1000 \text{ K}$  and  $p = 10^5 \text{ Pa}$ ? Please calculate with 4 significant figures.

.....  
See Chapter 9, Subsection “Enthalpy Dependence on Temperature”:

$$\begin{aligned} H &= H_0 + \int_{T_0}^T c_p dT = H_0 + \int_{T_0}^T (a + bT + cT^2) dT \\ &= H_0 + \left[ aT + \frac{1}{2}bT^2 + \frac{1}{3}cT^3 \right]_{298}^{1000} \\ &= 0 + [27.7(1000 - 298) + \frac{1}{2} \times 0.8 \times 10^{-3}(1000^2 - 298^2) \\ &\quad + \frac{1}{3} \times 10^{-6}(1000^3 - 298^3)] \\ &= 20,130 \text{ kJ K}^{-1} \text{ kmole}^{-1}. \end{aligned}$$

See Chapter 9, Subsection “Free Energy Dependence on Temperature”.

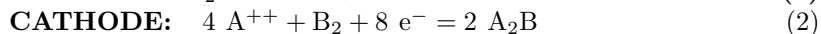
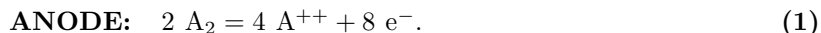
$$\begin{aligned} dS &= c_p \frac{dT}{T} - R \frac{dp}{p} \quad \underbrace{\quad}_{\substack{\text{const.} \\ \text{press.}}} \quad c_p \frac{dT}{T}. \\ S &= S_0 + \int_{T_0}^T \frac{c_p}{T} dT \\ &= S_0 + \int_{T_0}^T \left( \frac{a}{T} + b + cT \right) dt \\ &= S_0 + \left[ a \ln T + bT + \frac{1}{2}cT^2 \right]_{298}^{1000} \\ &= 130.0 + \left[ 27.7 \ln \frac{1000}{298} + 0.8 \times 10^{-3}(1000 - 298) \right. \\ &\quad \left. + \frac{10^{-6}}{2}(1000^2 - 298^2) \right] = 164.6 \text{ kJ K}^{-1} \text{ kmole}^{-1}. \end{aligned}$$

$$G = H - TS = 20,130 - 1000 \times 164.6 = -144.5 \times 10^3 \text{ kJ kmole}^{-1}.$$

At 1000 K and 100,000 Pa, the gas has:  
Enthalpy: 20.13 MJ per kilomole,  
Entropy: 164.6 kJ per K per kilomole,  
Free energy: -144.5 MJ per kilomole.

## Solution of Problem 9.6

**Prob 9.7** A fuel cell has the reactions:



All data are at RTP.

The overall reaction,  $2 \text{ A}_2 + \text{B}_2 = 2 \text{ A}_2\text{B}$ , releases 300 MJ per kmole of  $\text{A}_2\text{B}$  product in a calorimeter. The entropies of the different substances are:

$\text{A}_2$ : 200 kJ  $\text{K}^{-1}$  kmole $^{-1}$ ,

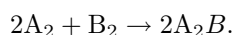
$\text{B}_2$ : 400 kJ  $\text{K}^{-1}$  kmole $^{-1}$ ,

$\text{A}_2\text{B}$ : 150 kJ  $\text{K}^{-1}$  kmole $^{-1}$ .

$\text{A}_2$  and  $\text{B}_2$  are gases, whereas  $\text{A}_2\text{B}$  is liquid.

- a. What is the voltage of an ideal fuel cell that uses the above reaction at RTP?

.....  
The overall reaction of the fuel-cell is



The reactant entropy is  $2 \times 200 + 400 = 800$  kJ/K; that of the product is  $2 \times 150 = 300$  kJ/K. The entropies associated with the materials in the reaction decreased by 500 kJ/K for each 2 kmole of the product,  $\text{A}_2\text{B}$  or

$$\Delta S = 250 \quad \text{kJ K}^{-1} \quad \text{per kmole of A}_2\text{B}.$$

To satisfy the second law of thermodynamics (under reversible conditions), an amount,  $T\Delta S$ , of heat must be generated:

$$T\Delta S = 298 \times 250 = 74.5 \quad \text{MJ per kmole of A}_2\text{B}.$$

The change in free energy owing to the reaction is

$$\Delta G = \Delta H - T\Delta S = -300 + 74.5 = -225.5 \quad \text{MJ per kmole of A}_2\text{B}.$$

8 electrons circulate in the load for every 2 molecules of  $\text{A}_2\text{B}$  formed, or 4 electrons/molecule:

$$V = \frac{-\Delta G}{n_e q N_0} = \frac{225.5}{4 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{26}} = 0.584 \quad \text{V}.$$

The reversible voltage of the cell is 0.584 V.

- b. Estimate the voltage at standard pressure and 50 C.  
.....

## Solution of Problem 9.7



The rate of change of the reversible voltage with temperature (at constant pressure) is

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{V + \frac{\Delta H}{n_e q N_0}}{T} = \left(0.584 + \frac{-300 \times 10^6}{4 \times 6.022 \times 10^{26} \times 1.6 \times 10^{-19}}\right) \frac{1}{298}$$

$$= -0.649 \times 10^{-3} \quad \text{V/K.}$$

$$V_{50\text{ C}} = 0.584 - 0.649 \times 10^{-3}(50 - 25) = 0.568 \quad \text{V.}$$

At 50 C, the reversible voltage of the cell is 0.568 V.

**c. How much heat does the ideal fuel cell produce per kilomole of A<sub>2</sub>B, at RTP?**

The ideal fuel-cell will generate 74.5 MJ of heat per kilomole of A<sub>2</sub>B produced.

**d. What is the voltage of the cell if the gases are delivered to it at 100 MPa? The operating temperature is 25 C.**

The energy of isothermal compression is free energy and will, therefore, affect the voltage.

Compress 2 kilomoles of A<sub>2</sub> from 0.1 MPa to 100 MPa:

$$W_{\text{compr}_{A_2}} = 2RT \ln \frac{p}{p_0} = 2 \times 8314 \times 298 \ln 10^3 = 34.2 \quad \text{MJ.}$$

Compress 1 kilomole of B<sub>2</sub> from 0.1 MPa to 100 MPa:

$$W_{\text{compr}_{B_2}} = 1 \times 8314 \times 298 \ln 10^3 = 17.1 \quad \text{MJ.}$$

The total energy used up in compressing the input gases is

$$W_{\text{compr}} = 34.2 + 17.1 = 51.3 \quad \text{MJ/per 2 kmols.}$$

Per kilomole,  $W_{\text{compr}} = 25.6$  MJ.

Since the product is liquid, it is not affected by the pressure change.

The energy used in compressing the gases isothermally is added to the free energy of the reaction or, correspondingly, causes a voltage increase of

$$V_{\text{compr}} = \frac{25.6 \times 10^6}{n_e q N_0} = 0.066 \quad \text{V,}$$

hence,

$$V_{25\text{ C}, 100\text{ MPa}} = 0.584 + 0.066 = 0.651 \quad \text{V.}$$

At 25 C, 100 MPa, the reversible voltage of the cell is 0.651 V.

## Solution of Problem 9.7

- e. If the internal resistance of the cell (operating at RTP) is  $0.001\ \Omega$ , what is the maximum power the cell can deliver to a load?

.....  
A generator will deliver maximum energy to a load if the latter matches the internal resistance of the former, i.e., if  $R_L = R_{int}$ . Then, the current will be  $I_L = V_{rev}/(R_L + R_{int}) = V_{rev}/2R_{int}$ . The corresponding power delivered to the load is

$$I_L^2 R_L = I_L^2 R_{int} = \frac{V_{rev}^2}{4R_{int}} = \frac{0.584^2}{4 \times 0.0001} = 85.3 \quad \text{W.}$$

The maximum power the cell can deliver to the load is 85.3 W.
---

- 
- f. What is the fuel consumption rate of the cell under these circumstances?
- 

Under maximum power, the current is

$$I_L = \frac{V_{rev}}{2R_{int}} = \frac{0.584}{2 \times 0.001} = 292 \quad \text{A.}$$

This current corresponds to 292 coulombs/second or  $1.82 \times 10^{21}$  electrons/second. Each molecule of  $A_2$  releases 4 electrons, hence the consumption rate of  $A_2$  is

$$\frac{\partial[A_2]}{\partial t} = \frac{1.82 \times 10^{21}}{4} = 445 \times 10^{18} \quad \text{molecules/s.}$$

or

$$\frac{\partial[A_2]}{\partial t} = 757 \times 10^{-9} \quad \text{kmoles/s.}$$

At maximum power, the cell consumes $757 \times 10^{-9}$ kilomoles of $A_2$ per second.
---

- 
- g. What is the efficiency of the cell?
- 

.....  
At 300 MJ/kilomole and at the above rate of consumption of  $A_2$ , the input power is

$$P_{in} = 757 \times 10^{-9} \times 300 \times 10^6 = 227.1 \quad \text{W.}$$

The efficiency is

$$\eta = \frac{85.3}{227.1} = 0.38.$$

At maximum power, the efficiency of the cell is 38%.
--

---

## Solution of Problem 9.7

**Prob 9.8** Owing to its ceramic electrolyte, a fuel cell can operate at 827 C. Pure oxygen is used as oxidizer. The gases are fed to the cell at a pressure of 1 atmosphere.

Use the data below:

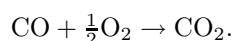
	$\Delta \bar{h}_f^\circ$	$\Delta \bar{g}_f^\circ$	$\gamma$	$\bar{s}^\circ$
	MJ	MJ		kJ K <sup>-1</sup>
	/kmol	/kmol		/kmol
CO(g)	-110.54	-137.28	1.363	197.5
CO <sub>2</sub> (g)	-393.51	-394.38	1.207	213.7
O <sub>2</sub> (g)	0	0	1.341	205.0

The values of  $\gamma$  are those appropriate for the the 25 C to 827 C interval.

We want to examine the influence of temperature on the performance of an ideal fuel cell.

- a. Calculate the reversible voltage and the efficiency of the above (ideal) cell at both 25 C and 827 C.

.....  
The overall reaction is



At 25 C (RTP conditions) the  $\Delta \bar{g}$  of the reaction is

$$\begin{aligned}\Delta \bar{g}_{\text{REACTION}} &= \Delta \bar{g}_{\text{CO}_2} - \Delta \bar{g}_{\text{CO}} - \frac{1}{2}\Delta \bar{g}_{\text{O}_2} \\ &= -394.38 - (-137.28) - \frac{1}{2} \times 0 = -257.10 \quad \text{MJ/kmol.}\end{aligned}$$

Since oxygen is divalent, 4 electrons will circulate in the load for each O<sub>2</sub> molecule. Hence, there will be 2 electrons per CO<sub>2</sub> molecule.

$$V_{\text{rev}} = \frac{|\Delta \bar{g}_{\text{REACTION}}|}{n_e q N_0},$$

$$V_{\text{rev}} = \frac{257.10 \times 10^6}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 1.334 \quad \text{V.}$$

The reversible voltage of the cell, at RTP, is 1.334 V.

At 25 C (RTP conditions) the  $\Delta \bar{h}$  of the reaction is

$$\begin{aligned}\Delta \bar{h}_{\text{REACTION}} &= \Delta \bar{h}_{\text{CO}_2} - \Delta \bar{h}_{\text{CO}} - \frac{1}{2}\Delta \bar{h}_{\text{O}_2} \\ &= -393.51 - (-110.54) - \frac{1}{2} \times 0 = 282.97 \quad \text{MJ/kmol.}\end{aligned}$$

## Solution of Problem 9.8

The efficiency is

$$\eta = \frac{\Delta \bar{g}}{\Delta \bar{h}} = \frac{257.10}{282.97} = 0.908.$$

The efficiency at RTP is 90.8%

As a first step in estimating the conditions at 827 C, we have to calculate the values of  $\Delta \bar{h}_f$  and  $\Delta \bar{g}_f$  for 827 C (1100 K) and 1 atmos. For this, we need to know the values of  $c_p$ .

$$c_p = R \left( 1 + \frac{1}{\gamma - 1} \right).$$

This yields

	J K <sup>-1</sup> kmol <sup>-1</sup>
CO	31,213
CO <sub>2</sub>	48,496
O <sub>2</sub>	32,690

The enthalpy of formation at the new temperature is

$$\Delta \bar{h}_f = \Delta \bar{h}_f^\circ + c_p \Delta T.$$

resulting in

$$\Delta \bar{h}_{fCO} = -110.54 \times 10^6 + 31,213 \times (1100 - 298) = -85.50 \times 10^6 \quad \text{MJ/kmol},$$

$$\Delta \bar{h}_{fCO_2} = -393.51 \times 10^6 + 48,496 \times (1100 - 298) = -354.62 \times 10^6 \quad \text{MJ/kmol},$$

and

$$\Delta \bar{h}_{fO_2} = 0 + 32,690 \times (1100 - 298) = 26.22 \times 10^6 \quad \text{MJ/kmol}.$$

The free energy at the new temperature is

$$\Delta \bar{g}_f = \Delta \bar{g}_f^\circ + (c_p - \bar{s}^\circ) \Delta T - T c_p \ln \frac{T}{T_0}.$$

resulting in

$$\begin{aligned} \Delta \bar{g}_{fCO} &= -137.28 \times 10^6 + (31.213 - 197.5) \times 10^3 \times (1100 - 298) \\ &\quad - 1100 \times 31.213 \times 10^3 \times \ln \left( \frac{1100}{298} \right) = -315.52 \times 10^6 \quad \text{MJ/kmol}. \end{aligned}$$

## Solution of Problem 9.8

$$\begin{aligned}\Delta\bar{g}_{f_{CO_2}} &= -394.38 \times 10^6 + (48.496 - 213.7) \times 10^3 \times (1100 - 298) \\ &\quad - 1100 \times 48.496 \times 10^3 \times \ln\left(\frac{1100}{298}\right) = -596.53 \times 10^6 \text{ MJ/kmol.}\end{aligned}$$

$$\begin{aligned}\Delta\bar{g}_{f_{O_2}} &= 0 + (32.690 - 205.0) \times 10^3 \times (1100 - 298) \\ &\quad - 1100 \times 32.690 \times 10^3 \times \ln\left(\frac{1100}{298}\right) = -185.18 \times 10^6 \text{ MJ/kmol.}\end{aligned}$$

The sum of the free energy of the reactants is

$$\begin{aligned}\sum \Delta\bar{g}_{f_{REACTANTS}} &= (-315.52) + \frac{1}{2}(-185.18) \\ &= -408.11 \text{ MJ/kmole } (CO)_2.\end{aligned}$$

and that of the product is

$$\sum \Delta\bar{g}_{f_{PRODUCT}} = -596.53 \text{ MJ/kmole of } CO_2.$$

Thus,

$$\Delta\bar{g}_{REACTION} = -596.53 - (-408.11) = -188.42 \text{ MJ/kmole } (CO_2)$$

$$V_{rev} = \frac{|\Delta\bar{g}_{REACTION}|}{n_e q N_0},$$

$$V_{rev} = \frac{188.42 \times 10^6}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 0.978 \text{ V.}$$

The reversible voltage of this cell is 0.978 V.

The sum of the enthalpies of the reactants is

$$\sum \Delta\bar{h}_{f_{REACTANTS}} = -85.50 + \frac{1}{2}26.22 = -72.39 \text{ MJ per kmole of } CO_2$$

and that of the product is

$$\sum \Delta\bar{h}_{f_{PRODUCT}} = -354.62 \text{ MJ/kmole of } CO_2$$

Thus,

$$\Delta\bar{h}_{REACTION} = -354.62 - (-72.39) = -282.23 \text{ MJ/kmole of } CO_2$$

The ideal efficiency of the cell is

$$\eta_{IDEAL} = \frac{\Delta\bar{g}}{\Delta\bar{h}} = \frac{-188.42}{-282.23} = 0.668.$$

## Solution of Problem 9.8

The ideal efficiency of this cell is 66.8%.

- 
- b. As expected (if you did the calculations correctly), you will have found that both  $V_{rev}$  and  $\eta$  are larger at the lower temperature. Yet, the cell is operated at 827 C where its ideal performance is not as good. Why? Explain in some detail.**

.....  
At low temperatures, the ceramic fuel cell using CO as fuel encounters two major difficulties:

1. The kinetics of the reaction become extremely slow even with good catalysts (expensive). Platinum-based catalyst are easily poisoned by CO.
  2. The ion conductivity of the ceramic electrolyte becomes negligible, even using low temperature ceramics such as samarium-doped ceria. In fact, at 298 K, the fuel cell would, essentially, deliver no power.
- 

## Solution of Problem 9.8

**Prob 9.9** A fuel cell was tested in the laboratory and yielded the following:

Open-circuit voltage	0.600 V
Internal resistance	0.01 $\Omega$
Voltage ( $I = 1$ A)	0.490 V
Voltage ( $I = 10$ A)	0.331 V

Thermodynamic data indicate that the reversible voltage of the fuel cell is 0.952 V and that the enthalpy change of the reaction is 1.26 times the reaction free energy. Two electrons circulate in the load per molecule of product.

Assume the Tafel Equation is valid. The internal resistance given above is the slope of the straight line portion of the  $v-i$  characteristic of the cell.

- a. What is the power the cell delivers to a load when the current is 5 A?

.....  
From Subsection 9.8.3 of the Textbook,

$$V_{oc} = V_L + IR_{int} + V_{act}. \quad (1)$$

From the Tafel equation,

$$V_{act} = V_1 + V_2 \ln I. \quad (2)$$

Let us calculate the constants  $V_1$  and  $V_2$ .

From the data in the problem,

$$V_{oc} = 0.6 \text{ V}, \quad \text{and} \quad R = 0.01 \text{ } \Omega.$$

$$\text{For } I = 1 \text{ A}, \quad 0.6 = 0.49 + 1 \times 0.01 + V_{act_1}, \quad \text{hence} \quad V_{act_1} = 0.1 \text{ V}.$$

Using this value in Equation 2,

$$0.1 = V_1 + V_2 \ln(1) \quad \text{or} \quad V_1 = 0.1 \text{ V}. \quad (3)$$

$$\text{For } I = 10 \text{ A}, \quad 0.6 = 0.331 + 10 \times 0.01 + V_{act_2}, \quad \text{hence} \quad V_{act_2} = 0.169 \text{ V}.$$

Again, using Equation 2,

$$0.169 = 0.1 + V_2 \ln(10) \quad \therefore \quad V_2 = 0.030 \text{ V}. \quad (4)$$

Consequently, the Tafel equation for this fuel cell is

$$V_{act} = 0.1 + 0.03 \ln I. \quad (5)$$

## Solution of Problem 9.9

When the current is 5 A (as required by the problem), the activation voltage is

$$V_{act} = 0.1 + 0.03 \ln(5) = 0.148 \quad \text{V.} \quad (6)$$

and the load voltage (from Equation 1), is

$$V_L = V_{oc} - V_{act} - R_{int}I = 0.6 - 0.148 - 0.01 \times 5 = 0.402 \quad \text{V.} \quad (7)$$

The power delivered to the load is

$$P_L = V_L I = 0.402 \times 5 = 2.01 \quad \text{W.} \quad (8)$$

The power delivered to the load is 2.01 W.

**b. What is the heat power dissipated internally when 5 A are being delivered?**

.....  
The heat power generated by the cell is the total input power owing to the hydrogen/oxygen reaction minus the power delivered to the load.

The reaction delivers a power,  $|\Delta H|\dot{N}$ .

From the problem statement,

$$\Delta H = 1.26\Delta G,$$

hence  $|\Delta H|\dot{N} = 1.26|\Delta G|\dot{N}$ .

$$|\Delta G| = qn_e N_0 V_{rev} = 1.60 \times 10^{-19} \times 2 \times 6.02 \times 10^{-26} \times 0.952 = 183.7 \quad \text{MJ.}$$

The rate of water production (the same as the rate of hydrogen consumption) is

$$\dot{N} = \frac{I}{qn_e N_0} = \frac{5}{1.60 \times 10^{-19} \times 2 \times 6.02 \times 10^{-26}} = 25.9 \times 10^{-9} \quad \text{kmoles/sec.} \quad (9)$$

As a result, the input power is

$$P_{in} = 1.26 \times 183.7 \times 25.9 \times 10^{-9} = 5.99 \quad \text{W,} \quad (10)$$

and the rate of heat generation in the cell is

$$P_{heat} = P_{in} - P_L = 5.99 - 2.01 = 3.98 \quad \text{W.} \quad (11)$$

When the load current is 5 A, 3.99 W are dissipated internally.

## Solution of Problem 9.9



**Prob 9.10** A hydrogen-oxygen fuel cell, operating at RTP, has the following  $v$ - $i$  characteristics:

$$V_L = 0.8 - 0.0001I_L.$$

Assume 100% current efficiency.

- a. What is the hydrogen consumption rate (in mg/s) when the cell delivers 1 kW to a load?

.....  
From the  $V$ - $I$  characteristics, we observe that

$$V_{oc} = 0.8 \quad \text{V},$$

and

$$R_{int} = 0.0001 \quad \Omega.$$

When a load,  $R_L$ , is connected to the fuel cell, a current,  $I$ , circulates:

$$I = \frac{V_{oc}}{R_{int} + R_L} = \frac{0.8}{0.0001 + R_L}.$$

The power delivered to the load is

$$P_L = I^2 R_L = \left( \frac{0.8}{0.0001 + R_L} \right)^2 R_L = 1000 \quad \text{W}.$$

From this,

$$R_L^2 - 4.4 \times 10^{-4} R_L + 10^{-8} = 0$$

The roots of this quadratic equation are

$$R_L = \begin{cases} 4.16 \times 10^{-4} & \Omega \\ 0.24 \times 10^{-4} & \Omega \end{cases}$$

Thus, there are two values of the load resistance that allow the fuel-cell to deliver 1000 W. The lower value results in a larger current and, consequently in larger internal losses in the cell. Let us use the value,  $R_L = 4.16 \times 10^{-4} \Omega$ .

The current delivered by the cell is

$$I = \frac{0.8}{1 \times 10^{-4} + 4.16 \times 10^{-4}} = 1550 \quad \text{A}.$$

This current corresponds to 1550 coulombs/s or a flow of  $1550/1.6 \times 10^{-19} = 9.677 \times 10^{21}$  electrons per second.

Since each  $\text{H}_2$  releases 2 electrons, the current above corresponds to a consumption of  $4.838 \times 10^{21}/6.02 \times 10^{26} = 8.03 \times 10^{-6}$  kilomoles of hydrogen per second or  $16.1 \times 10^{-6}$  kg of  $\text{H}_2$  or 16.1 mg of hydrogen per second.

## Solution of Problem 9.10

The hydrogen consumption rate when 1000 W are delivered to the load is 16.1 mg/s.

**b. What is the heat generated by the cell? Liquid water is produced.**

.....  
The short answer is:

The rate of enthalpy change when  $\dot{N} = 8.03 \times 10^{-6}$  kilomoles of hydrogen per second combine with oxygen forming liquid water is

$$P_{in} = |\Delta H_f^\circ| \dot{N} = 285.9 \times 10^6 \times 8.03 \times 10^{-6} = 2300 \quad \text{W.}$$

The power output is, as stated in the problem, 1000 W. Hence, the heat produced by the cell is  $2300 - 1000 = 1300$  W.

If you want a detailed account of the sources of heat, consider:

Assume the cell produces water vapor which then is condensed before being exhausted.

- The reversible voltage at RTP (when water vapor is produced) is  $V_{rev} = 1.185$  V. The open-circuit voltage is 0.8 V. Under a 1550 A current,  $P_{oc} = (1.185 - 0.8) \times 1550 = 596.8$  W.
- The Joule losses are  $P_{Joule} = 1550^2 \times 0.0001 = 240.3$  W.
- The thermodynamic heat rejected is  $P_{therm} = 298 \times 44.4 \times 10^3 \times 8.03 \times 10^{-6} = 106.2$  W.
- Water vapor condenses in the cell.  $P_{cond} = 44.1 \times 10^6 \times 8.03 \times 10^{-6} = 354.1$  W.

The sum of these four heat rates is 1297 W close enough to the 1300 W found earlier. The small discrepancy comes from the approximate value of the vaporization heat we used.

You may also wish to assume that the fuel cell generates liquid water. Then:

- b.1 The reversible voltage at RTP (when liquid water is produced) is  $V_{rev} = 1.231$  V. The open-circuit voltage is 0.8 V. Under a 1550 A current,  $P_{oc} = (1.231 - 0.8) \times 1550 = 668.1$  W.
- b.2 The Joule losses are  $P_{Joule} = 1550^2 \times 0.0001 = 240.3$  W.
- b.3 The thermodynamic heat has now changed because the entropy of liquid water is less than that of water vapor. It is  $163.2 \text{ kJ K}^{-1} \text{ kmole}^{-1}$ . Thus the loss of entropy associated with the matter balance of the hydrogen plus oxygen to liquid water reaction is  $163.4 \text{ kJ K}^{-1} \text{ kmole}^{-1}$ . The associated heat generated at 298 K is 48.7 MJ/kmole. The heat generation rate owing to this process is  $48.7 \times 10^6 \times 8.03 \times 10^{-6} = 391.1$  W.

## Solution of Problem 9.10

The heat of condensation has already been taken into account (the fuel cell generates liquid water). The sum of the three heat rates above is 1300 W, as before.

The heat released by the fuel-cell when 1000 W are delivered to the load is 1300 W.

---

Solution of Problem 9.10

**Prob 9.11** A fuel cell is prismatic in shape and measures  $d \times 2d \times 2d$  (where  $d = 33$  cm). It is fed with  $\text{H}_2$  and  $\text{O}_2$  which are admitted at 25 C and 1 atmosphere. Product water is exhausted at 1 atmosphere and 110 C.

The inside of the cell is evenly at 110 C. The outside is maintained at 50 C by immersing it totally in running water admitted at 20 C and exhausted at 45 C. Liquid water has a heat capacity of 4 MJ per K per  $\text{m}^3$ . Assume that the temperature gradient across the walls is uniform. The walls are made of 10-mm thick stainless steel with a heat conductivity of 70 W per m per K. The only energy input to the cell comes from the fuel gases admitted. Heat is removed by both the coolant water and the product water that is exhausted from the cell at a rate of  $\dot{N}$  kmol/s.

The load voltage is  $V_L = 0.9 - R_{int}I$  volts.  $R_{int} = 10^{-7} \Omega$ . To simplify the solution, assume that the fuel cell reaction proceeds at RTP and liquid water is produced at 25 C. This water is then heated up so that the exhaust is at the 110 C prescribed.

a. What heat energy is removed every second by the coolant water?

.....  
The surface area of the fuel cell casing is  $A = 16d^2 = 1.74 \text{ m}^2$ . The temperature differential between the inside and the outside of the cell is  $\Delta T = 60$  K. Since the 10 mm ( $\Delta x = 0.01$  m) thick wall has a thermal conductivity of  $\lambda = 70 \text{ W m}^{-1} \text{ K}^{-1}$ , the heat power,  $P_{coolant}$ , removed from the cell by the coolant water is

$$P_{coolant} = \lambda A \frac{\Delta T}{\Delta x} = 70 \times 1.74 \frac{60}{10 \times 10^{-3}} = 730,800 \text{ W}.$$

The coolant water removes 730.8 kW of heat.

---

b. What is the flow rate of the coolant water?

.....  
The above heat power is removed by  $\dot{V} \text{ m}^3/\text{s}$  of water with a temperature rise of  $\Delta T = 45 - 20 = 25$  K.

$$\dot{V} = \frac{P_{coolant}}{4 \times 10^6 \Delta T} = \frac{730,800}{4 \times 10^6 \times 25} = 0.0073 \text{ m}^3/\text{s}.$$

The flow rate of the coolant water is 7.3 liters/s.

---

c. Express the heat removal rate by the product water in terms of  $\dot{N}$ .

.....

## Solution of Problem 9.11

Water is produced by the reaction at a rate,  $\dot{N}$ , kilomoles per second. This means that the reactants are used up at a rate of  $\dot{N}$  kilomoles per second of hydrogen and  $\frac{1}{2}\dot{N}$  kilomoles per second of oxygen. Notice that  $\dot{N}$  kilomoles/s of water correspond to  $18\dot{N}$  kg/s of water or (in liquid form) to  $0.018\dot{N}$  m<sup>3</sup>/s of water.

The product water is generated at the temperature of the incoming fuels (25 C). It is then heated up to 100 C—a  $\Delta T$  of 75 K—when it boils. The water vapor is superheated to 110 C, an additional  $\Delta T$  of 10 K.

Under the above assumptions, the heat removing action of the product water has three components:

- raising the water temperature by 75 K;
- causing the water to change phase from liquid to vapor;
- raising the vapor temperature by 10 K.

Heating the water uses a power

$$P_{\text{heating, liquid}} = 4 \times 10^6 \times 75 \times 0.018\dot{N} = 5.4 \times 10^6 \dot{N} \quad \text{W.}$$

The heat of vaporization of water at 1 atmosphere and 100 C is about  $2.2 \times 10^6$  J/kg<sup>†</sup>. The evaporation of  $18\dot{N}$  kg/s of water requires a power of

$$P_{\text{boiling}} = 2.2 \times 10^6 \times 18\dot{N} = 39.6 \times 10^6 \dot{N} \quad \text{W.}$$

Water vapor has a heat capacity of 36 kJ per K per kilomole. Thus the heat absorbed in heating the water vapor is

$$P_{\text{heating, vapor}} = 36 \times 10^3 \times 10 \times \dot{N} = 0.4 \times 10^6 \dot{N} \quad \text{W.}$$

The total heat carried away by the product water is

$$P_{\text{product}} = 45.4 \times 10^6 \dot{N} \quad \text{W.}$$

The heating of the water vapor removes a negligible amount of energy.

The heat removal rate of the product water is  $45.4 \times 10^6 \dot{N}$  W.

#### d What is the input power in terms of $\dot{N}$ ?

.....  
The enthalpy of formation of liquid water is  $-285.9$  MJ/kmole. The input power is  $P_{\text{in}} = 285.9 \times 10^6 \dot{N}$  W.

The input power is  $285.9 \times 10^6 \dot{N}$  W.

---

<sup>†</sup> In the Textbook (Subsection 9.7.1), the heat of vaporization is listed as 44.1 MJ/kmole or 2.45 MJ/kg. This is at 25 C; the more accurate value at 100 C is found in the CRC. See also inset in Section 9.7.1.

## Solution of Problem 9.11

e., f. & g. What is the power delivered to the load in terms of  $\dot{N}$ ? Write an equation for thermal equilibrium of the cell using your results from above. What is the value of  $I$  that satisfies the above equation?

.....  
The power delivered to the load is the input power minus the heat power removed:

$$\begin{aligned} P_{load} &= P_{in} - P_{coolant} - P_{product} \\ &= 285.9 \times 10^6 \dot{N} - 730,800 - 45.4 \times 10^6 \dot{N} \\ &= 240.5 \times 10^6 \dot{N} - 730,800 \quad \text{W.} \end{aligned}$$

However, the power in the load is also

$$P_{load} = I_L V_L = 0.9 I_L - 10^{-7} I_L^2.$$

In addition,

$$I_L = q n_e N_0 \dot{N} = 193 \times 10^6 \dot{N},$$

from which

$$\dot{N} = 5.182 \times 10^{-9} I_L.$$

Combining these equations,

$$0.9 I_L - 10^{-7} I_L^2 = 240.5 \times 10^6 \times 5.182 \times 10^{-9} I_L - 730,800,$$

$$10^{-7} I_L^2 - 0.9 I_L + 240.5 \times 10^6 \times 5.182 \times 10^{-9} I_L - 730,800 = 0$$

The positive root of this equation is  $I = 1.48 \times 10^6$  A. This corresponds to a hydrogen consumption rate of  $7.67 \times 10^{-3}$  kilomoles/second and an electric power in the load of

$$P_L = 0.9 \times 1.48 \times 10^6 - 10^{-7} \times (1.48 \times 10^6)^2 = 1.12 \times 10^6 \quad \text{W.}$$

The load current is 1.48 MA  
The fuel consumption rate is 0.0077 kmol/s.  
The power in the load is 1.12 MW.

## Solution of Problem 9.11

**Prob 9.12** A hydrogen/oxygen fuel cell has a cooling system that allows accurate measurement of the heat dissipated and precisely controls the operating temperature which is kept, under all circumstances, at 298 K.

When a current of 500 A is generated, the cooling system removes 350 W of heat, while when the current is raised to 2000 A, the amount of heat removed is 2000 W.

Estimate the heat removed when the current is 1000 A. The input gases are at RTP and liquid water is created in the process.

Assume a linear dependence of the load voltage on the load current.

.....  
The heat generated by the cell has four components: the thermodynamic heat (owing to the need to balance the entropies of the products with that of the reactants), the Joule losses, the losses owing to the difference between the reversible voltage and the open-circuit voltage, and the heat released by the condensation of product water because the water that exits the cell is in the liquid state according to the problem statement.

$$\begin{aligned} P_{heat} &= T|\Delta S|\dot{N} + R_{int}I^2 + (V_{rev} - V_{oc})I + |\Delta H_{vap}|\dot{N} \\ &= (T|\Delta S| + |\Delta H_{vap}|)\dot{N} + R_{int}I^2 + (V_{rev} - V_{oc})I \end{aligned} \quad (1)$$

A current of  $I$  amperes corresponds to a water production rate of  $\dot{N}$  kilomoles per second:

$$\dot{N} = \frac{I}{2qN_0} = \frac{I}{2 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{26}} = \frac{I}{192.7 \times 10^6}.$$

Hence,

$$P_{heat} = (T|\Delta S| + |\Delta H_{vap}|)\frac{I}{192.7 \times 10^6} + R_{int}I^2 + (V_{rev} - V_{oc})I.$$

From Section 9.7.2,

$$|T\Delta S| = 13.2 \times 10^6 \quad \text{J per kilomole of H}_2\text{O},$$

and

$$V_{rev} = 1.185 \quad \text{V}.$$

$$\begin{aligned} P_{heat} &= \frac{(13.2 \times 10^6 + 44.1 \times 10^6)}{192.7 \times 10^6}I + R_{int}I^2 + (1.185 - V_{oc})I \\ &= (0.2974 + 1.185 - V_{oc})I + R_{int}I^2 = (1.482 - V_{oc})I + R_{int}I^2. \end{aligned} \quad (2)$$

Using the two pairs of  $P_{heat}$  and  $I$  values,

## Solution of Problem 9.12

$$\begin{cases} 350 = (1.482 - V_{oc}) \times 500 + R_{int} \times 500^2, \\ 2000 = (1.482 - V_{oc}) \times 2000 + R_{int} \times 2000^2. \end{cases}$$

This yields

$$\begin{aligned} R_{int} &= 200 \times 10^{-6} \quad \text{ohms and} \\ V_{oc} &= 0.882 \quad \text{V}, \end{aligned}$$

so that

$$P_{heat} = 0.60I + 200 \times 10^{-6}I^2 \quad (3)$$

It is possible to solve this problem without going into the details of the heat production mechanisms.

$$P_{heat} = P_{in} - P_L,$$

$$P_{in} = |\Delta H| \dot{N} = \frac{|\Delta H|}{2qN_0} I = \frac{285.9 \times 10^6}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} I = 1.482I,$$

$$P_L = V_L I = (V_{oc} - R_{int}I)I = V_{oc}I - R_{int}I^2,$$

$$P_{heat} = 1.482I - V_{oc}I - R_{int}I^2 = (1.482 - V_{oc})I - R_{int}I^2.$$

This equation is the same as Equation 2 derived previously and, of course, leads to the same values of  $R_{int}$  and  $V_{oc}$  and also leads to Equation (3).

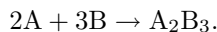
Plugging in  $I = 1000$  A,  $P_{heat} = 800$  W.

When the fuel cell delivers 1000 A, it generates 800 W of heat.

## Solution of Problem 9.12



**Prob 9.13** An ideal fuel cell operates at 1000 K. Two reactant gases (not necessarily hydrogen and oxygen) are fed in at 1 atmosphere. The reversible voltage is 1.00 V. What will the voltage be if gas A is fed in at 100 atmospheres and gas B at 200 atmospheres, both still at 1000 K? The reaction is



The product is liquid (in spite of the high temperature). A total of 6 electrons circulate in the load for each molecule of product.†

.....  
The energy to isothermally compress the reactants is

$$\begin{aligned} W_{\text{compr}} &= 2RT \ln \frac{p_A}{p_{A_0}} + 3RT \ln \frac{p_B}{p_{B_0}} = RT \ln \frac{p_A^2 p_B^3}{p_{A_0}^2 p_{B_0}^3} \\ &= 8314 \times 1000 \times \ln(100^2 \times 200^3) = 208.7 \times 10^6 \quad \text{J.} \end{aligned}$$

All this is free energy and will appear as electric output.  
Since the product is liquid, it is incompressible.

$$\begin{aligned} V &= \frac{\Delta G}{n_e q N_0} = \frac{\Delta G_0}{n_e q N_0} + \frac{208.7 \times 10^6}{n_e q N_0} \\ &= 1 + \frac{208.7 \times 10^6}{6 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 1.36 \quad \text{V.} \end{aligned}$$

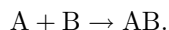
Voltage with high pressure feed is 1.36 V.
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† The very large difference in pressure between the two reactant gases would require a strong diaphragm or electrolyte. This suggests a ceramic electrolyte and hence the high operating temperature. Clearly, the realizability of this fuel cell is highly doubtful.

## Solution of Problem 9.13

**Prob 9.14** A fuel cell employs the reaction below,



At STP, the relevant thermodynamic data are

	$\Delta \bar{h}_f^\circ$ MJ/kmole	$\bar{s}$ kJ/(K kmole)
A(g)	0	100
B(g)	0	150
AB(g)	-200	200

**What is the reversible voltage of the above fuel cell? For each molecule of AB, 2 electrons circulate in the load.**

.....  
The enthalpy of formation,  $\Delta \bar{h}_f^\circ$ , of AB is -200 MJ/kmole.

The entropy of the reactants is  $100 + 150 = 250 \text{ kJ K}^{-1}\text{kmole}^{-1}$ , while that of the product is  $200 \text{ kJ K}^{-1}\text{kmole}^{-1}$ . Thus, the reaction causes the disappearance of 50,000 entropy units. Since, in a close system, entropy cannot decrease, an amount  $\bar{q} = T\Delta\bar{s} = 298.15 \times 50,000 = 14,408,000 \text{ J/kmole}$ , of heat must be generated.

$$Q = 298 \times (-50,000) = -14,900,000 \text{ MJ/kmole of product.}$$

$$\Delta G = \Delta H - T\Delta S = -200 - (-14.9) = -185.1 \text{ MJ/kmole of product.}$$

$$V = \frac{\Delta G}{n_e q N_0} = \frac{185.1 \times 10^6}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 0.961 \text{ V.}$$

The reversible voltage is 0.961 V.

Solution of Problem 9.14

**Prob 9.15** A fuel cell battery is to be used in a satellite power supply. It must deliver a steady 2 kW at 24 V for 1 week. The mass of the cell must be the minimum possible.

The fuel cell manufacturer has a design with the following characteristics:

**Open-circuit voltage: 1.10 V,**

**Internal resistivity:  $92 \times 10^{-6}$  ohm  $\text{m}^2$ ,**

**Cell mass: 15 kg per  $\text{m}^2$  of active electrode area.**

**There is a linear relationship between  $V_L$  and  $I_L$ .**

**How many cells must be connected in series?**

**What is the total mass of all fuel cells in the battery?**

.....  
The voltage,  $V$ , delivered by each cell depends on the current density:

$$V = 1.1 - 92 \times 10^{-6} J.$$

The power the cell delivers (per unit active electrode area) is

$$P = VJ = 1.1J - 92 \times 10^{-6} J^2.$$

For minimum mass, each cell must deliver maximum power,

$$\frac{\partial P}{\partial J} = 1.1 - 2 \times 92 \times 10^{-6} J = 0,$$

From this,  $J_{max} = 5980 \text{ A/m}^2$ .

At this current density, the voltage delivered by each cell is

$$V = 1.1 - 92 \times 10^{-6} \times 5980 = 0.55 \text{ V}.$$

This is, of course, one half of the open-circuit voltage and there was no need to go through the calculations above, except that we needed to find the current density.

To form a battery with 24 V output (full load), we need  $N$  cells:

$$N = \frac{24}{0.55} = 43.5 \rightarrow 44 \text{ cells}.$$

To deliver 2 kW, this battery has to furnish  $2000/24 = 83.3$  A. Since the cells are in series, this is also the current through each cell.

The active area of the cell is

$$A = \frac{I}{J} = \frac{83.3}{5980} = 0.014 \text{ m}^2.$$

At 15 kg/ $\text{m}^2$ , each cell masses 0.209 kg, and the battery masses 9.2 kg.

## Solution of Problem 9.15

The battery consists of 44 cells in series and masses 9.2 kg.

There are other solution strategies that can be used.

1 - Since the power that the battery has to deliver is 2,000 watts under a voltage of 24 volts, the current must be

$$I = \frac{2000}{24} = 83.3 \quad \text{A.}$$

The active surface of each cell must be

$$A = \frac{83.3}{J},$$

and the mass of the battery is

$$M = 15AN$$

where  $N$  is the number of cells in the battery. Hence,

$$M = 15 \times 83.3 \frac{N}{J} = 1250 \frac{N}{J},$$

$$V = 1.1 - 92 \times 10^{-6} J,$$

$$M = \frac{1250 \times 92 \times 10^{-6} N}{1.1 - V} = \frac{0.115N}{1.1 - V},$$

$$NV = 24,$$

$$M = \frac{0.115}{1.1 - 24/N} = \frac{0.115N^2}{1.1N - 24} \quad (1).$$

To minimize  $M$ ,

$$\frac{d}{dN} \left( \frac{0.115N^2}{1.1N - 24} \right) = \frac{2 \times 0.115N}{1.1N - 24} - \frac{0.115N^2}{(1.1N - 24)^2} = 0.$$

Solving for  $N$ , we find  $N \approx 44$ , as before. From Equation 1,

$$M = \frac{0.115 \times 44^2}{1.1 \times 44 - 24} = 9.2 \quad \text{kg.}$$

2 - Since a battery of  $N$  cells must deliver 24 V at 83.3 A, we have

$$\frac{24}{N} = 1.1 - \frac{92 \times 10^{-6} \times 83.3}{A}, \quad (1)$$

which leads to

$$NA = \frac{0.00767}{1.1 - 24N} \quad (2)$$

For minimum battery mass,  $nA$  must be a minimum and this occurs when  $N = 44$ .

## Solution of Problem 9.15

**Prob 9.16** The open circuit voltage of a hydrogen/oxygen fuel cell operating at RTP is 0.96 V and its internal resistance is 1.2 m $\Omega$ . The activation voltage drop is given by

$$V_{act} = 0.031 + 0.015 \ln I,$$

where  $I$  is in amperes.

From thermodynamic data, the reversible voltage,  $V_{rev}$ , is known to be 1.185 V.

200 of the above cells are connected in series forming a battery that feeds a resistive load rated at 2.5 kW at 100 V.

What is the actual load voltage?

How much heat does the battery generate internally if the water is exhausted in vapor form?

.....  
Since the load is rated as 2500 W at 100 V, its resistance must be

$$R_L = \frac{V_{L_{rated}}^2}{P_{L_{rated}}} = \frac{100^2}{2500} = 4.0 \quad \Omega,$$

Let  $V_L$  be the actual load voltage. Then,

$$V_L = n(V_{oc} - I_L R - 0.031 - 0.015 \ln I_L),$$

where  $n = 200$  is the number of cells in the battery and  $I_L$  is the actual load current.

$$I_L = \frac{V_L}{R_L},$$

$$V_L = I_L R_L = 4I_L,$$

$$\frac{4I_L}{200} = 0.96 - 0.0012I_L - 0.031 - 0.015 \ln I_L,$$

$$I_L = 43.82 - 0.7076 \ln I_L. \quad (1)$$

Clearly,  $I_L$  must be somewhat smaller than 43.82 A. Assume,  $I_L = 40$  A, then  $0.7076 \ln I_L = 2.61$ . Since  $\ln I_L$  changes much slower than  $I_L$ , assume it remains constant. Then,

$$I_L = 43.82 - 2.61 = 42.21 \quad \text{A.}$$

Iterate using  $0.7076 \ln I_L = 2.63$ ,

$$I_L = 43.82 - 2.63 = 41.2 \quad \text{A,}$$

$$V_L = R_L I_L = 4 \times 41.2 = 164.8 \quad \text{V.}$$

## Solution of Problem 9.16

The load voltage is 164.8 V.

The internal voltage drops are  $V_{drop_{total}} = (V_{rev} - V_{oc}) + IR + V_{act}$ ,

$$V_{rev} - V_{oc} = 1.185 - 0.96 = 0.225 \quad \text{V},$$

$$IR = 41.2 \times 0.0012 = 0.0494 \quad \text{V},$$

$$V_{act} = 0.031 + 0.015 \ln 41.2 = 0.0868 \quad \text{V},$$

$$V_{drop_{total}} = 0.225 + 0.0494 + 0.0868 = 0.361 \quad \text{V},$$

Thus, the heat power generated by the losses in the cell is

$$P_{loss_{cell}} = 0.361 \times 41.2 = 14.9 \quad \text{W},$$

In addition there is the thermodynamic heat released,

$$P_{thermodynamic} = T\Delta S\dot{N}.$$

At RTP, the  $|T\Delta S|$  product for a hydrogen-oxygen fuel cell is 13.2 MJ/kmole. Hence,

$$P_{thermodynamic} = 13.2 \times 10^6 \dot{N}.$$

$$\dot{N} = \frac{I_L}{qn_e N_0} = 5.18 \times 10^{-9} \times 41.2 = 213 \times 10^{-9} \quad \text{kmole/s},$$

$$P_{thermodynamic} = 13.2 \times 10^6 \times 213 \times 10^{-9} = 2.82 \quad \text{W}.$$

Thus, the total heat power released is  $14.9 + 2.8 = 17.7 \quad \text{W/cell}$  or 3536 W/battery.

The battery generates 3536 W of heat internally.

## Solution of Problem 9.16

**Prob 9.17** A fuel cell battery is fed by  $\text{H}_2$  and  $\text{O}_2$  (both at 300 K) and produces water vapor that promptly condenses inside the cell.

$\Delta T$  is the difference, in kelvins, between the temperature of the active area of the cell and 300 K, which is supposed to be the temperature of the cooling liquid and of the environment.

Two main mechanisms remove heat from the cells:

- Some heat is conducted away at a rate of 40 W per  $\text{m}^2$  of active electrode surface for each kelvin of  $\Delta T$ . This, of course, implies some cooling system whose exact nature is irrelevant as far as this problem is concerned.
- To simplify the solution, assume that water vapor is synthesized in the cell at the temperature of the incoming gases (300 K) and then immediately condenses at this temperature and then heats up by an amount  $\Delta T$  to reach the operating temperature of the cell. The water is then removed, carrying with it a certain amount of heat and, thus, cooling the cell. If the temperature of the product water exceeds 100 C, assume that the cell is pressurized so that water does not boil. However, assume that all the reactions actually occur at RTP, i.e., use thermodynamic data for RTP.

The  $V$ - $J$  characteristic of the cell is

$$V = 1.05 - 95.8 \times 10^{-6} J,$$

where  $J$  is the current density in  $\text{A}/\text{m}^2$ .

The current efficiency is 100%.

Although the cell will operate at conditions that differ from RTP, use RTP thermodynamic data to simplify the problem.

- a. The battery is not going to be operated at full power because it probably will exceed the maximum allowable temperature. Nevertheless, calculate what the equilibrium temperature would be if full power operation were attempted.

.....  
At full power, the load voltage will be half the open circuit voltage because full power is transferred when the load resistance equals the internal resistance. Thus,  $V_{load} = 0.525$  V.

$$0.525 = 1.05 - 95.8 \times 10^{-6} J, \quad (1)$$

Since  $J = I/S$  where  $S$  is the active area of the cell, Equation 1 can be written as

$$0.525 = 1.05 - \frac{95.8 \times 10^{-6}}{S} I, \quad (2)$$

## Solution of Problem 9.17

and

$$I = \frac{(1.05 - 0.525) \times S}{95.8 \times 10^{-6}} = 5480 \times S. \quad (3)$$

A current of  $5480 \times S$  amperes corresponds to

$$\begin{aligned} \dot{N} &= \frac{I}{n_e q N_0} = \frac{5480 \times S}{2 \times 1.60 \times 10^{-19} \times 6.02 \times 10^{-26}} \\ &= 28.4 \times 10^{-6} \times S \quad \text{kmoles of H}_2\text{O per s.} \end{aligned} \quad (4)$$

Since it is stipulated that the product water condenses in place thereby depositing its heat of vaporization in the cell, the heat power input to each cell is

$$P_{in} = 285.9 \times 10^6 \times 28.4 \times 10^{-6} \times S = 8120 \times S \quad \text{W.}$$

Power,  $P_{out}$ , is removed from the cell by three mechanisms:

- electric power,  $P_{load}$ , delivered to the load,
- heat power,  $P_{conduction}$ , removed by conduction,
- heat power,  $P_{convection}$ , necessary to raise the temperature of the product water which is removed from the cell.

$$\text{Formally,} \quad P_{out} = P_{load} + P_{conduction} + \underset{\substack{\text{by liquid} \\ \text{water}}}{P_{convection}} \quad (5)$$

The power delivered to the load is

$$P_{load} = 0.525 \times 5480 \times S = 2877 \times S. \quad \text{W}$$

The power conducted away is

$$P_{conduction} = 40\Delta T \times S \quad \text{W.} \quad (6)$$

The power necessary to raise the temperature of the product water is

$$\underset{\substack{\text{by liquid} \\ \text{water}}}{P_{convection}} = \underbrace{4200}_{\substack{\text{J kg}^{-1} \text{K}^{-1}}} \times \underbrace{28.4 \times 10^{-6}}_{\substack{\text{kmole s}^{-1} \text{m}^{-2}}} \times \underbrace{18}_{\substack{\text{kg/kmole}}} \times \Delta T \times S = 2.1\Delta T \times S, \quad (7)$$

where  $4200 \text{ J kg}^{-1} \text{ K}^{-1}$  is the heat capacity of water.

$$P_{out} = P_{in} = 8120 \times S = 2877 \times S + 40\Delta T \times S + 2.1\Delta T \times S, \quad (8)$$

## Solution of Problem 9.17



$$\Delta T = 124 \quad \text{K}, \quad (9)$$

$$T = 424 \quad \text{K}. \quad (10)$$

At full power, the battery temperature would reach 424 K.

This, of course, exceeds the boiling temperature of water at 1 atmosphere. It is highly probable that the cell will be destroyed by full power operation.

**b. In fact, the battery will operate at a much lower power. It must deliver 20 kW to a load at 12 V. It must consist of several cells connected in series. The mass of each cell is 15 kg for each m<sup>2</sup> of active electrode area.**

**The battery must deliver this power for a week. The total mass (fuel plus battery) must be minimized. Ignore the mass of the fuel tanks.**

**How many cells must be employed?**

**What is the total mass?**

**How many kg of H<sub>2</sub> and how many of O<sub>2</sub> are needed?**

**What is the operating temperature of the cell?**

.....  
The current the battery must deliver is

$$I = \frac{20,000}{12} = 1667 \quad \text{A}. \quad (11)$$

Since the  $N$  cells are in series, this is also the current through each cell. Consequently, the voltage of each cell (at nominal load) is  $V = 12/N$ .

The H<sub>2</sub> consumption, per cell, is

$$\begin{aligned} \dot{N}_{H_2} &= \frac{I}{qn_e N_0} = \frac{1667}{1.60 \times 10^{-19} \times 2 \times 6.02 \times 10^{-26}} \\ &= 8.6 \times 10^{-6} \quad \text{kmoles (H}_2\text{)/s}, \end{aligned} \quad (12)$$

$$8.6 \times 10^{-6} \quad \text{kmoles (H}_2\text{)/s} = 17.3 \times 10^{-6} \quad \text{kg (H}_2\text{)/s} \quad (13)$$

For each kilomole of H<sub>2</sub>, half a kilomole of O<sub>2</sub> is needed, and since the molecular mass of the latter is 16 times that of the former, the O<sub>2</sub> consumption rate (measured in kg/s) must be 8 times that of H<sub>2</sub>,

$$\dot{N}_{O_2} = 8 \times 17.3 \times 10^{-6} = 138.2 \times 10^{-6} \quad \text{kg (O}_2\text{)/s}. \quad (14)$$

The total gas consumption rate, per cell, is

$$\begin{aligned} \dot{N}_T &= (17.3 + 138.2) \times 10^{-6} = 155.5 \times 10^{-6} \quad \text{kg (gases)/s}. \\ &= 155.5 \times 10^{-6} \times 3600 \times 24 \times 7 = 94.0 \quad \text{kg (gases)/week}. \end{aligned} \quad (15)$$

## Solution of Problem 9.17

The total gas consumption rate, per battery, is

$$\dot{N}_{TB} = 94.0N \quad \text{kg (fuel)/week.} \quad (16)$$

Let  $M_G = 94.0N$  be the mass of gases used in a week by the battery, and let  $M_B$  be the mass of the battery, itself

$$M_B = 15 \times S \times N, \quad (17)$$

where  $S = I/J$  is the active area of the electrodes in one cell.

$$M_B = 15 \frac{I}{J} N = 25,000 \frac{N}{J}, \quad (18)$$

$$V = 1.05 - 95.8 \times 10^{-6} J = \frac{12}{N}, \quad (19)$$

$$J = 10,960 - \frac{125,300}{N}, \quad (20)$$

$$M_B = \frac{2.28N^2}{N - 11.43}. \quad (21)$$

The overall mass is

$$M_T = M_B + M_G = \frac{2.28N^2}{N - 11.43} + 94N. \quad (22)$$

Find the minimum value of  $M_T$ .

$$\frac{dM_T}{dN} = 94 + \frac{4.56N}{N - 11.43} - \frac{2.28N^2}{(N - 11.43)^2} = 0, \quad (23)$$

$$96.3N^2 - 2201N + 12,281 = 0, \quad (24)$$

$$N = \frac{2201 \pm \sqrt{2201^2 - 4 \times 96.3 \times 12,281}}{192.6} = \frac{2201 \pm 341.6}{192.6} = \begin{cases} 13.2, \\ 9.6. \end{cases} \quad (25)$$

This suggests that the number of cells must be either 10 or 13. Putting  $N = 10$  into Equation 20, leads to a negative value for  $J$ . Thus the correct solution must be  $N = 13$  which leads to  $J = 1322 \text{ A/m}^2$  and an active area of  $1667/1322 = 1.26 \text{ m}^2$ .

A total of 13 cells is required.

From Equation 22 we calculate a total mass of 1467 kg.

The mass of the battery plus consumables is 1467 kg.  
This does not include the mass of the fuel tanks.

The hydrogen consumption is  $17.3 \times 10^{-6} \text{ kg/s}$  or 10.4 kg/week.  
The oxygen consumption is  $138.2 \times 10^{-6} \text{ kg/s}$  or 83.7 kg/week.

## Solution of Problem 9.17

Redoing the temperature calculation (all the powers below are per cell),

$$P_{in} = 285.9 \times 10^6 \times 8.6 \times 10^{-6} = 2459 \quad \text{W.} \quad (26)$$

The power delivered to the load is

$$P_{load} = \frac{20,000}{13} = 1538. \quad \text{W.} \quad (27)$$

The power conducted away is

$$P_{conduction} = 40\Delta T \times S = 40 \times 1.26 \times \Delta T = 50.4\Delta T \quad \text{W.} \quad (28)$$

The power necessary to raise the temperature of the product water is

$$P_{convection} = \underbrace{4200}_{\substack{\text{by liquid} \\ \text{water}}} \times \underbrace{8.6 \times 10^{-6}}_{\substack{\text{J kg}^{-1} \text{K}^{-1}}} \times \underbrace{18}_{\substack{\text{kmole/s} \\ \text{kg/kmole}}} \times \Delta T = 0.65\Delta T, \quad (29)$$

$$P_{out} = P_{in} = 2459 = 1538 + 50.4\Delta T + 0.65\Delta T, \quad (30)$$

$$\Delta T = 18.0 \quad \text{K}, \quad (31)$$

$$T = 318 \quad \text{K}. \quad (32)$$

The operating temperature of the cell is 318 K.

It can be seen that to minimize the total mass, it is important to increase the efficiency (i.e., reduce the fuel consumption) by operating at a much lower current density than that which leads to maximum power.

---

## Solution of Problem 9.17

**Prob 9.18** Fill in the answers as follows:

If output voltage rises, mark “R,” if it falls, mark “F,” if there is no effect, mark “N.”

	IDEAL FUEL CELL	PRACTICAL FUEL CELL
Higher temperature		
Higher reactant pressure		
Higher product pressure		

---

	IDEAL FUEL CELL	PRACTICAL FUEL CELL
Higher temperature	$\mathcal{F}$	$\mathcal{R}$
Higher reactant pressure	$\mathcal{R}$	$\mathcal{R}$
Higher product pressure	$\mathcal{F}$	$\mathcal{F}$

---

Solution of Problem 9.18

**Prob 9.19** A fuel cell, generating water vapor, has a straight line  $v$ - $i$  characteristic:

$$V_L = V_0 - R_{int}I$$

Both  $V_0$  and  $R_{int}$  are temperature dependent and are given by the expressions below, over the temperature range of interest.

$$V_0 = \beta_0(1 + \alpha_V T)V_{rev},$$

$$R_{int} = (1 + \alpha_R T)R_{int0}.$$

The coefficients are:

$$\begin{aligned}\beta_0 &= 0.677, \\ \alpha_V &= 443.5 \times 10^{-6} \quad \text{per K}, \\ R_{int0} &= 0.00145 \quad \Omega, \\ \alpha_R &= -1.867 \times 10^{-3} \quad \text{per K}.\end{aligned}$$

What are the efficiencies of the fuel cell at 298 K and at 500 K when feeding a 1 milliohm load?

.....  
At 298 K,  $V_{rev} = 1.185$  V (from Text).

At 500 K, the free energy change of the water synthesis reaction is -219.3 MJ/kmole (see Example 2 in Chapter 9 of the Text). Thus,

$$V_{rev} = \frac{219.4 \times 10^6}{2 \times 1.60 \times 10^{-19} \times 6.02 \times 10^{26}} = 1.138 \quad \text{V}.$$

$$V_{0298} = 0.677(1 + 443.5 \times 10^{-6} \times 298) \times 1.185 = 0.908 \quad \text{V}.$$

$$V_{0500} = 0.677(1 + 443.5 \times 10^{-6} \times 500) \times 1.138 = 0.941 \quad \text{V}.$$

$$R_{int298} = (1 - 1.867 \times 10^{-3} \times 298) \times 0.00145 = 643 \times 10^{-6} \quad \Omega,$$

$$R_{int500} = (1 - 1.867 \times 10^{-3} \times 500) \times 0.00145 = 96 \times 10^{-6} \quad \Omega.$$

$$V_{L298} = 0.908 - 643 \times 10^{-6}I,$$

$$V_{L500} = 0.941 - 96 \times 10^{-6}I,$$

$$I_{L298} = \frac{0.908 - 643 \times 10^{-6}I_{L298}}{0.001} \quad \therefore \quad I_{L298} = 552.6 \quad \text{A},$$

$$I_{L500} = \frac{0.941 - 96 \times 10^{-6}I_{L500}}{0.001} \quad \therefore \quad I_{L500} = 858.6 \quad \text{A},$$

$$P_{L298} = R_L \times I_{L298}^2 = 305.4 \quad \text{W}$$

$$P_{L500} = R_L \times I_{L500}^2 = 737.2 \quad \text{W},$$

**Solution of Problem 9.19**

$$\dot{N}_{298} = \frac{I_{L_{298}}}{2qN_0} = \frac{552.6}{2 \times 1.60 \times 10^{-19} \times 6.02 \times 10^{-26}} = 2.87 \times 10^{-6} \text{ kmol/s},$$

$$P_{in_{298}} = 241.8 \times 10^6 \times 2.87 \times 10^{-6} = 694.0 \text{ W},$$

$$\eta_{298} = \frac{305.4}{694.0} = 0.440,$$

$$\dot{N}_{500} = \frac{I_{L_{500}}}{2qN_0} = \frac{858.6}{2 \times 1.60 \times 10^{-19} \times 6.02 \times 10^{-26}} = 4.45 \times 10^{-6} \text{ kmol/s},$$

See Example 1 in Chapter 9 of the text:

$$P_{in_{500}} = 243.7 \times 10^6 \times 4.45 \times 10^{-6} = 1084 \text{ W},$$

$$\eta_{298} = \frac{737.2}{1084} = 0.680.$$

The efficiencies are 44.0% and 68.0%,  
respectively at 298 K and 500 K.

## Solution of Problem 9.19

**Prob 9.20** A fuel cell battery is to be used aboard the space station. The bus voltage (the voltage the battery has to deliver under full load) is 24 V when delivering 30 kW. Since the space craft has a hydrogen and oxygen supply, the battery will use these gases which are delivered to it at 1 atmosphere and 298 K.

A manufacturer-submitted sample cell was tested in the laboratory with the following results:

When no current is drawn from the cell, its voltage is 1.085 V. When delivering 2000 A, the voltage is 0.752 V. A straight line relationship was found to exist between  $V$  and  $I$ .

The cell masses 75 kg and, when taken apart, it was found that the active electrode area is  $1.5 \text{ m}^2$ .

It is clear that if the battery is to deliver 30 kW under 24 V, it must generate a current of 1250 A. Since all the cells are in series, this is also the current through each cell.

The sample cell operates with a current density of  $1250/1.5 = 833.3 \text{ A/m}^2$ . If the manufacturer constructs a cell, in all aspects identical to the sample, except with different active electrode area,  $S$ , the new cell must still deliver the 1250 A but under different current density and, consequently, under different cell load voltage. Since the battery load voltage must still be 24 V, the battery will contain a different number,  $N$ , of cells.

Assume that the mass of the new cell is proportional to the active area of the electrodes.

The total mass (mass,  $M_B$ , of the battery plus mass,  $M_F$ , of the fuel,  $\text{H}_2$  and  $\text{O}_2$ ) is to be minimized for a 30-day long mission during which the battery delivers a steady 30 kW at 24 V.

Ignore the mass of the fuel tanks. The current efficiency is 100%.

- a. Calculate this minimum total mass. How many cells are needed in series?

.....  
Since there is a straight line relationship between voltage and current in this cell, the load voltage can be described by

$$V_L = V_{oc} - R_{int}I. \quad (1)$$

The value of  $V_{oc}$  was given as 1.085 V, and, for  $I = 2000 \text{ A}$ ,  $V_L = 0.752 \text{ V}$ , so that

$$0.752 = 1.085 - 2000R_{int} \quad (2)$$

from which

$$R_{int} = \frac{1.085 - 0.752}{2000} = 166.4 \times 10^{-6} \Omega \quad (3)$$

Since the fuel cell to be used will be a scaled model of the sample cell submitted by the manufacturer, it is useful to write the  $V_L$  equation in terms of the current density,  $J$ .

## Solution of Problem 9.20

The active area of the sample cell was given as  $1.5 \text{ m}^2$ , hence, the current density is  $J = I/1.5$ , or,  $I = 1.5J$ . Thus, one can write

$$V_L = 1.085 - 1.5 \times 166.4 \times 10^{-6} J = 1.085 - 250 \times 10^{-6} J \quad (4)$$

When in operation aboard the space station (delivering 30 kW under 24 V), the current through each cell (the same as the current through the battery) is, under all circumstances, 1250 A. Because the rate of fuel consumption depends only on the current (if the current efficiency is 100%), in all cases, the fuel consumption of each individual cell is the same. However, since the number of cells in the battery depends on the active area of the electrode, the fuel consumption of the battery is, itself a function of the electrode area.

The  $\text{H}_2$  consumption, per cell, is

$$\begin{aligned} \dot{N}_{\text{H}_2} &= \frac{I}{qn_e N_0} = \frac{1250}{1.6 \times 10^{-19} \times 2 \times 6.022 \times 10^{26}} \\ &= 6.5 \times 10^{-6} \text{ kmoles } (\text{H}_2)/\text{s}, \end{aligned} \quad (5)$$

$$6.5 \times 10^{-6} \text{ kmoles } (\text{H}_2)/\text{s} = 13.0 \times 10^{-6} \text{ kg } (\text{H}_2)/\text{s}. \quad (6)$$

For each kilomole of  $\text{H}_2$ , half a kilomole of  $\text{O}_2$  is needed, and since the molecular mass of the latter is 8 times that of the former,

$$\dot{N}_{\text{O}_2} = 8 \times 13 \times 10^{-6} = 104 \times 10^{-6} \text{ kg } (\text{O}_2)/\text{s}. \quad (7)$$

The total fuel consumption rate, per cell, is

$$\dot{N}_T = (13 + 104) \times 10^{-6} = 117 \times 10^{-6} \text{ kg(fuel)/s}. \quad (8)$$

or

$$117 \times 10^{-6} \times 3600 \times 24 \times 30 = 303 \text{ kg (fuel)/(30 day)}. \quad (9)$$

The total fuel consumption rate, in a battery of  $N$  cells, is

$$\dot{N}_{TB} = 303N \text{ kg (fuel)/(30 day)}. \quad (10)$$

Let  $M_F = \dot{N}_{TB} = 303N$  be the mass of fuel used in 30 days by the battery, and let  $M_B$  be the mass of the battery, itself

Per unit active surface area, each cell masses  $\frac{75}{1.5} = 50 \text{ kg/m}^{-2}$  and the whole battery masses

$$M_B = 50NS. \quad (11)$$

Since  $S = I/J$ ,

$$M_B = 50N \frac{I}{J} = 62,500 \frac{N}{J}, \quad (12)$$

## Solution of Problem 9.20



The load voltage is

$$V = 1.085 - 250 \times 10^{-6} J = \frac{24}{N}, \quad (13)$$

from which a relationship between  $N$  and  $J$  can be established:

$$J = 4,340 - \frac{96,000}{N}, \quad (14)$$

This allows elimination of  $J$  from Equation 12,

$$M_B = \frac{14.4N^2}{N - 22.12}. \quad (15)$$

The overall mass is

$$M_T = M_B + M_F = \frac{14.4N^2}{N - 22.12} + 303N. \quad (16)$$

Find the minimum value of  $M_T$ .

$$\frac{dM_T}{dN} = 303 + \frac{28.8N}{N - 22.12} - \frac{14.4N^2}{(N - 22.12)^2} = 0, \quad (17)$$

$$317.4N^2 - 14,042N + 148,260 = 0, \quad (18)$$

$$N^2 - 44.24N + 467.1 = 0, \quad (19)$$

$$N = \frac{44.24 \pm \sqrt{44.24^2 - 4 \times 467.1}}{2} = \frac{44.24 \pm 9.42}{2} = \begin{cases} 26.9, \\ 17.4. \end{cases} \quad (20)$$

Take  $N = 27$  which leads (Equation 16) to a total mass of 10,330 kg.

A total of 27 cells is required.

The mass of the battery plus fuel is 10,330 kg.  
This does not include the mass of the fuel tanks.

If we had chosen  $N = 17$ , Equation 14 would lead to a negative (unacceptable) value for  $J$ .

- 
- b. In the cell above, assume that water is synthesized as vapor at the temperature of the incoming gases (298 K) and promptly condenses into a liquid and then heats up to  $T_{op}$ , the operating**

## Solution of Problem 9.20

temperature of the device. The product water is continuously removed from the cell at this latter temperature.

In addition, a cooling system also removes heat. It does this at a rate of 6 W per degree of temperature difference ( $T_{op} - 298$  K) for each square meter of active electrode surface.

What is  $T_{op}$  when the battery delivers 30 kW as in the first part of this problem?

.....  
The calculation below is for one cell of the battery.

The rate of water production is the same as that of hydrogen consumption and is  $6.5 \times 10^{-6}$  kmole ( $\text{H}_2\text{O}$ )/s which corresponds to  $18 \times 6.5 \times 10^{-6} = 117 \times 10^{-6}$  kg ( $\text{H}_2\text{O}$ )/s. Since the heat capacity of water is about 4200 J  $\text{kg}^{-1} \text{K}^{-1}$ , the heat removed by the product water is

$$P_{water} = 4,200 \times 117 \times 10^{-6} \times \Delta T = 0.49\Delta T, \quad (21)$$

where  $\Delta T \equiv T_{op} - 298$ .

The heat removed by the cooling system is

$$P_{cooling} = 6 \times S \times \Delta T. \quad (22)$$

We need to find  $S$ .

$$J = 4,340 - \frac{96,000}{N} = 784 \quad \text{A/m}^2, \quad (23)$$

because  $N = 27$ .

$$S = \frac{I}{J} = \frac{1,250}{784} = 1.59 \quad \text{m}^2, \quad (24)$$

$$P_{cooling} = 9.54\Delta T. \quad (25)$$

The total heat removed from the cell is  $(0.49 + 9.54)\Delta T = 10.0\Delta T$ .

This amount of heat must equal the difference between the total power input to the cell,  $P_{in}$ , and the electric power,  $P_L$ , delivered by the cell.

Since it is stipulated that the product water condenses in inside the cell thereby depositing there its heat of vaporization, the cell power input is

$$P_{in} = 285.9 \times 10^6 \times 6.5 \times 10^{-6} = 1,858 \quad \text{W}. \quad (26)$$

$P_L$  per cell is  $30,000/27 = 1111$  W.

Thus the net heat production in each cell  $P_{heat} = 1,858 - 1111 = 747$  W

$$10.0\Delta T = 747, \quad (27)$$

$$\Delta T = 74.7 \quad \text{K}, \quad (28)$$

$$T_{op} = 298 + 74.2 = 372.7 \quad \text{K} \quad \text{or} \quad 99.6 \quad \text{C}. \quad (29)$$

The battery operates at 99.6 C.

---

## Solution of Problem 9.20

**Prob 9.21** A hydrogen-oxygen fuel cell has the following characteristics when both reactants are supplied at the pressure of 1 atm:

$$V_{oc} = 0.75 + 0.0005T \quad \text{V} \quad R_{int} = 0.007 - 0.000015T \quad \Omega.$$

Estimate, roughly, the power this fuel cell delivers to a 5 milliohm load.

In any fuel cell, heat may be removed by

- circulation of a coolant,
- excess reactants that leave the cell at a temperature higher than the input temperature,
- products that leave the cell at a temperature higher than that at which they were synthesized.

To simplify this problem assume that the contribution of mechanism a is always 30 times that of mechanism c and that of mechanism b is negligible.

Assume that the reactants are fed in at 298.2 K and the product water is created as a vapor at this temperature and then heated to  $T_{op}$  by the heat rejected by the cell.

Pure hydrogen and pure oxygen are supplied at 1 atm.

- a. What is the temperature of the cell when temperature equilibrium has been reached?

.....  
The current through the load is

$$I = \frac{V_{oc}}{R_L + R_{int}} = \frac{0.75 + 0.0005T_{op}}{0.005 + 0.007 - 0.000015T_{op}} = \frac{50,000 + 33.33T_{op}}{800 - T_{op}} \quad (1)$$

where  $T_{op}$  is the operating temperature.

The power delivered to the load is

$$P_L = I^2 R_L = 0.005 I^2. \quad (2)$$

To make a rough estimate of this power we have to guess the operating temperature, realizing that the effect of this temperature is not too strong. Take, for instance,  $T_{op} = 60^\circ\text{C}$  or 333 K. Using Equation 1, we get  $I = 131$  A and a  $P_L = 86$  W.

We expect, roughly, 100 W to be delivered to the load.

The rate of water production is

$$\dot{N} = \frac{I}{qn_e N_0} = 5.19 \times 10^{-9} I. \quad (3)$$

The input power to the cell is

$$P_{in} = |\Delta H| \dot{N} = 5.19 \times 10^{-9} |\Delta H| I. \quad (4)$$

## Solution of Problem 9.21

The load power is

$$P_L = R_L I^2 = 0.005 I^2 \quad (5)$$

The heat rejected by the cell is

$$P_{heat} = P_{in} - P_L = 5.19 \times 10^{-9} |\Delta H| I - 5 \times 10^{-3} I^2. \quad (6)$$

The heat removed by the product water

$$\begin{aligned} P_{prod} &= c \dot{N} \Delta T = 5.19 \times 10^{-9} c (T_{op} - 298.2) I \\ &= 5.19 \times 10^{-9} \times 10^{-9} (T_{op} - 298.2) c I \end{aligned} \quad (7)$$

In the above,  $c$  is the heat capacity of 1 kilomole of water.

Since the coolant removes 30 times as much heat as the product water, the total heat removed is

$$\begin{aligned} P_{removed} &= 31 \times 5.19 \times 10^{-9} \times 10^{-9} (T_{op} - 298.2) c I \\ &= 160.9 \times 10^{-9} (T_{op} - 298.2) c I \end{aligned} \quad (8)$$

This must be equal to the heat generated.

$$160.9 \times 10^{-9} (T_{op} - 298.2) c I = 5.19 \times 10^{-9} |\Delta H| I - 5 \times 10^{-3} I^2 \quad (9)$$

or

$$I = 1.038 \times 10^{-6} |\Delta H| - 32.18 \times 10^{-6} (T_{op} - 298.2) c. \quad (10)$$

There are two situations to be considered:

- a1. Water vapor is formed and water vapor is exhausted.  
Under such conditions,

$$|\Delta H| = 241.8 \times 10^6 \quad \text{J/kmole},$$

$$c = 36 \times 10^3 \quad \text{J K}^{-1} \text{kmole}^{-1}.$$

Equation 10 becomes

$$I = 596.4 - 1.158 T_{op}. \quad (10_{vapor})$$

- a2. Liquid water is formed and liquid water is exhausted.  
Under such conditions,

$$|\Delta H| = 285.9 \times 10^6 \quad \text{J/kmole},$$

$$c = 72 \times 10^3 \quad \text{J K}^{-1} \text{kmole}^{-1}.$$

Equation 10 becomes

## Solution of Problem 9.21

$$I = 987.4 - 2.318T_{op}. \quad (10_{liquid})$$

We now have two independent equations that yield  $I$ —Equations 1 and 10. Combining them,

a1. Water vapor

$$\frac{50,000 - 33.33T_{op}}{800 - T_{op}} = 596.4 - 1.158T_{op}.$$

This leads to

$$T_{op}^2 - 1344T_{op} + 368,800 = 0.$$

The solutions are

$$T_{op} = \begin{cases} 959.7 \\ 384.3. \end{cases}$$

The lower temperature makes sense.

a2. Liquid water

$$\frac{50,000 - 33.33T_{op}}{800 - T_{op}} = 987.4 - 2.318T_{op}.$$

This leads to

$$T_{op}^2 - 1240T_{op} + 319,200 = 0.$$

The solutions are

$$T_{op} = \begin{cases} 875.3 \\ 364.7. \end{cases}$$

We notice that the lower of these two temperature is below the boiling point of water (373.2 K), hence, the cell can operate at 1 atmosphere of pressure and still deliver liquid water. So both conditions can be implemented.

The operating temperature of the cell is 384.3 K (111.1 C) if water vapor is produced and 364.7 K (91.5 C) if liquid water is produced.

**b. What is the load current and the power delivered to the load under the above conditions?**

.....  
Introducing  $T_{op} = 384.3$  K into Equation 10,  $I = 151$  A. This leads to  
a  $P_L = 0.005 \times 135.2^2 = 115$  W.

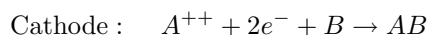
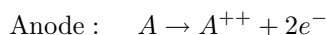
The load current is 151 A and the power is 115 W.

## Solution of Problem 9.21

## Prob 9.22

$R_L$	$I$
Ohms	Amps
0.05	14.98
0.10	8.23
0.15	5.71
0.20	4.37
0.25	3.54

The reactions in a fuel cell are:



The gases, A and B, are fictitious (and so are their properties). The atomic mass of A is 16 daltons and that of B is 18 daltons. Both A and B behave, over the temperature range of interest, as if they had 5 degrees of freedom, while the product, AB, as if it had 7.

The fuel cell was tested in a laboratory by observing the current delivered as the load resistance was altered.

The results are displayed in the table.

- a. What are the open circuit voltage and the internal resistance of the cell?

Clearly,  $V_L = IR_L$ , hence we can complete the table:

$R_L$	$I$	$V_L$
Ohms	Amps	Volts
0.05	14.98	0.749
0.10	8.23	0.823
0.15	5.71	0.857
0.20	4.37	0.875
0.25	3.54	0.885

The first question to be answered is whether the relationship between  $I$  and  $V_L$  is linear or not. To do this, let's make a linear regression using the two extreme data pairs (largest and smallest current) and then test to see if the remaining data pairs fall (roughly) on this line.

If the relationship is linear, then

$$V_L = V_{oc} - R_{int}I.$$

## Solution of Problem 9.22

We have

$$\begin{cases} 0.749 = V_{oc} - R_{int} \times 14.98, \\ 0.885 = V_{oc} - R_{int} \times 3.54. \end{cases}$$

from which

$$\begin{cases} V_{oc} = 0.927 & \text{V} \\ R_{int} = 0.0119 & \Omega \end{cases}$$

Thus,

$$V_L = 0.927 - 0.0119I$$

$I$ Amps Observed	$V_L$ Volts Observed	$V_L$ Volts Regression
14.98	0.749	0.749
8.23	0.823	0.829
5.71	0.857	0.859
4.37	0.875	0.875
3.54	0.885	0.885

Now, we have to check if this relationship is valid for the remaining data pairs. Applying the formula, we can predict the various  $V_L$  and compare them with the observed values. From the table, it is clear that all data pairs are a part of the same regression.

Thus, the activation voltage drop is negligible.

The open-circuit voltage is 0.927 V  
and the internal resistance is 0.0119 ohms.

**b. Careful calorimetric observations show that when the fuel cell is delivering 10.0 A to a load, the heat dissipated internally is 3.40 W.**

**From this information, determine the  $\Delta H$  of the reaction.**

.....  
The rate at which product AB is formed is given by

$$\dot{N} = \frac{I}{2qN_0} = \frac{10}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 51.82 \times 10^{-9} \quad \text{kmole/s.}$$

The energy input to the cell is

$$P_{in} = |\Delta \bar{h}| \dot{N},$$

while the power delivered to the load is

$$P_L = IV_L = 10 \times (0.927 - 0.0119 \times I) = 8.08 \quad \text{W.}$$

Consequently,

## Solution of Problem 9.22

$$P_{heat} = P_{in} - P_L,$$

$$|\Delta \bar{h}| = \frac{P_{heat} + P_L}{\dot{N}} = \frac{3.40 + 8.08}{51.82 \times 10^{-9}} = 221.5 \times 10^6 \quad \text{J/kmole.}$$

The enthalpy change owing to the reaction is  
-221.5 MJ per kilomole of AB.

- c. Notice that  $P_{heat}$  depends on  $(V_{rev} - V_{oc})I$ . This would suggest that it is possible to determine  $V_{rev}$  from the knowledge of  $P_{heat}$ . Demonstrate that it is not possible to do so, i.e., that for a fixed  $V_{oc}$  and  $R_{int}$ ,  $P_{heat}$  is not sensitive to the value of  $V_{rev}$ .

$$P_{heat} = (V_{rev} - V_{oc})I + T|\Delta \bar{s}|\dot{N} + R_{int}I^2,$$

$$\dot{N} = \frac{I}{2qN_0},$$

$$T|\Delta \bar{s}| = |\Delta \bar{h}| - |\Delta \bar{g}|,$$

$$V_{rev} = \frac{|\Delta \bar{g}|}{2qN_0}.$$

Combining these equations,

$$P_{heat} = |\Delta \bar{g}| \frac{I}{2qN_0} - V_{oc}I + |\Delta \bar{h}| \frac{I}{2qN_0} - |\Delta \bar{g}| \frac{I}{2qN_0} + R_{int}I^2.$$

$$P_{heat} = |\Delta \bar{h}| \frac{I}{2qN_0} + R_{int}I^2 - V_{oc}I.$$

Thus, the term  $V_{rev}I$  cancels the term  $|\Delta \bar{h}| \frac{I}{2qN_0}$ , and  $P_{heat}$  is the same for any  $\Delta \bar{g}$ .

- d. In order to estimate the  $\Delta \bar{g}$  of the reaction, an external voltage was applied to the fuel cell so as to cause it to act as an electrolyzer. When this external voltage was 1.271 V, the electrolyzed produced A at a rate of 2.985 g/hour. Making plausible assumptions, estimate the  $\Delta \bar{g}$  of the reaction.

2.985 g/hour correspond to  $829.2 \times 10^{-9}$  kg/s. Since the molecular mass of gas A is 16, this is equivalent to  $51.82 \times 10^{-9}$  kilomoles/s. We saw that this production rate results from a 10.0 A current.

## Solution of Problem 9.22



The electrolyzer, very probably, has the same internal resistance as the fuel cell, hence the voltage applied to it bears the following relationship with the current through it:

$$V = V_0 + R_{int}I.$$

From the data given in the problem:

$$1.271 = V_0 + 0.0119 \times 10,$$

from which,

$$V_0 = 1.152 \quad \text{V}.$$

Thus, as an electrolyzer, the highest voltage that leads to 0 current is 1.152 V, while as a fuel cell the zero current occurs when the voltage is 0.927 V. The difference between these voltages (0.225 V) must be twice the value of  $V_{rev} - V_{oc}$ . In other words,

$$V_{rev} = V_{oc} + \frac{0.225}{2} = 1.040 \quad \text{V}.$$

The free energy change owing to the reaction is

$$\Delta\bar{g} = -2qN_0V_{rev} = -2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26} \times 1.04 = -200.7 \times 10^6 \quad \text{J}.$$

The free energy change owing to the reaction is  
-200.7 MJ per kilomole of A.

## Solution of Problem 9.22

**Prob 9.23** A hydrogen/oxygen fuel cell has a  $V$ - $I$  characteristic (at RTP) given by

$$V_L = 0.98 - 10^{-3}I.$$

The active area of its electrodes is  $0.444 \text{ m}^2$ . The water is exhausted from the cell in gaseous form.

**a.1** What is the rate of heat production when the cell is open circuited?

When open-circuited, the cell delivers no electric output, hence it needs no fuel input and consequently dissipates no heat.

The fuel cell generates no heat.

**a.2** What is the rate of heat production when the cell is short circuited?

The  $V$ - $I$  characteristic is

$$V_L = 0.98 - 2.25 \times 10^{-3}I.$$

because  $R_{int}A = 10^{-3} \quad \Omega\text{m}^2$  and, consequently

$$R_{int} = \frac{10^{-3}}{0.444} = 0.00225 \quad \Omega$$

When short-circuited, the cell will deliver a current of

$$I_L = \frac{0.98}{0.00225} = 435 \quad \text{A.}$$

The rate of water production is

$$\dot{N} = \frac{I}{n_e q N_0} = \frac{435}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 2.26 \times 10^{-6} \quad \text{kmoles/s.}$$

The power input to the cell is

$$P_{in} = 241.8 \quad \text{MJ/kmole} \times 2.26 \times 10^{-6} \quad \text{kmoles/s.} = 545 \quad \text{W.}$$

Since the power delivered to the load is zero (because the load resistance is zero), all the input power is transformed into heat.

The fuel cell generates heat at the rate of 545 W.

## Solution of Problem 9.23

**a.3 What is the rate of heat production when the cell is connected to a load that maximizes the power output?**

.....  
The load that maximizes power output is one that matches the internal resistance of the cell, i.e.,

$$R_L = R_{int} = 0.00225 \quad \Omega.$$

The load current is then

$$I_L = \frac{0.98}{2 \times 0.00225} = 218 \quad \text{A}.$$

Such a current leads to a water production rate of half of that of the short-circuited case (because the current is one half of the short-circuit current):  $\dot{N} = 1.13 \times 10^{-6}$  kmol/s. The power input is also half of that in the preceding case:  $P_{in} = 272$  W.

The power delivered to the load is

$$P_L = I_L^2 R_L = 218^2 \times 0.00225 = 107 \quad \text{W}.$$

The heat dissipated inside the cell is

$$P_{heat} = P_{in} - P_L = 272 - 107 = 165 \quad \text{W}.$$

The fuel cell generates heat at the rate of 165 W.
--

---

**b. What are the efficiencies of the cell under the 3 conditions above?**

<p>The efficiency in case a) is undetermined because there is neither input nor output. The efficiency in case b) is zero because there is input but no output. The efficiency in case c) is <math>\eta = \frac{107}{272} = 0.393</math>.</p>
---

---

**c. What is the efficiency of the cell if it delivers half of its maximum power? Use the more efficient solution.**

.....  
Maximum power delivered to the load is 107 W. Half power is (approximately) 54 W.

The power the cell delivers to the load is

$$P_L = V_L I_L = 0.98 I_L - 2.25 \times 10^{-3} I_L^2 = 54.$$

From this quadratic equation, we obtain two solutions:

## Solution of Problem 9.23

$$I_L = 370.8 \text{ A corresponding to } V_L = 0.1457V,$$

and

$$I_L = 64.8 \text{ A corresponding to } V_L = 0.8342V.$$

Since the fuel consumption is proportional to the current, the first solution is less efficient than the second (both deliver the same electric output).

$$\dot{N} = \frac{64.8}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 336 \times 10^{-9} \quad \text{kmole/s.}$$

corresponding to

$$P_{in} = 336 \times 10^{-9} \times 241.8 \times 10^6 = 81.2 \quad \text{W.}$$

This leads to the excellent efficiency of

$$\eta = \frac{54}{81.2} = 0.665.$$

The efficiency is 66.5%

**d. Assume that  $V_{oc}$  is a constant fraction of  $V_{rev}$ . Thus, under all circumstances  $V_{oc} = (0.98/1.185) \times V_{rev} = 0.827V_{rev}$ . What is the  $V$ - $I$  characteristic of the cell when fed air at 1 atmos and 25 C instead of oxygen?**

.....  
The partial pressure of oxygen in air is 0.2 atmos. The energy to decompress half a mole of oxygen by a factor of 5, isothermally, is

$$|W_{decompress}| = |\mu RT \ln 0.2| = \left| \frac{1}{2} \times 8314 \times 298 \times (-1.61) \right| = 2 \quad \text{MJ.}$$

Thus, the free energy of the reaction becomes  $228.6 - 2 = 226.6$  MJ/kmole and the reversible voltage becomes

$$V_{rev} = \frac{226.6 \times 10^6}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 1.174 \quad \text{V,}$$

and the open-circuit voltage is

$$V_{oc} = 0.827 \times 1.174 = 0.971 \quad \text{V.}$$

## Solution of Problem 9.23

The  $V$ - $I$  characteristic is  
 $V_L = 0.971 - 2.25 \times 10^{-3} I_L$ .

- e. To simplify this problem assume that the only way to remove heat from the cell is via the exhaust stream which consists of water vapor and excess input gases. The input gases (hydrogen and air) are at 298 K. Assume that the water is produced at 298 K and then heated by the fuel cell to the exhaust temperature,  $T$ .

What is the value of  $T$  when the cell, fed by the minimum amount of air that satisfies the oxygen requirement of the device, produces the electric output of Item 3 (half its maximum power). Although the oxidizer is air, not pure oxygen, use, for simplicity, the  $V$ - $I$  characteristic for pure oxygen as given in Item 1.

Under the conditions of Item 3,  $P_{in} = 81.2$  W and  $P_L = 54$  W. Hence, the heat produced by the cell is  $P_{heat} = 81.2 - 54 = 27.2$  W.

The rate of water production is  $335.8 \times 10^{-9}$  kmole/s.

The rate of air inflow is 5 times that of the required oxygen which is  $335.8 \times 10^{-9} / 2 = 167.9 \times 10^{-9}$  kmole/s. Hence air flows in at a rate of  $839.5 \times 10^{-9}$  kmole/s. The nitrogen content is 80% of the above or  $671.6 \times 10^{-9}$  kmole/s. The oxygen is used up and is exhausted as water and thus has already been accounted for. The nitrogen acts as an additional coolant.

The heat removed is

$$P_{heat} = (c_{H_2O} \dot{N}_{H_2O} + c_{N_2} \dot{N}_{N_2}) \times \Delta T.$$

$c_{H_2O}$  is the heat capacity of water vapor and is about  $37 \times 10^3$  joules per kelvin per kilomole.

$c_{N_2}$  is the heat capacity of nitrogen and is about  $29 \times 10^3$  joules per kelvin per kilomole.

$$27.2 = (37,000 \times 335.8 \times 10^{-9} + 29,000 \times 671.6 \times 10^{-9}) \times \Delta T.$$

From the above, the temperature of the exhaust gases will be  $298 + 862 = 1160$  K.

The temperature of the exhaust gases will be 1160 K

- f. If you made no mistake, you have found that the temperature calculated in the preceding item is way too high. Much more

## Solution of Problem 9.23

vigorous cooling will be necessary. This can be accomplished by injecting much more air than is required by the stoichiometry. Assume that the temperature rise should not exceed 80 K. How much must the flow of air be compared with that required in Item 5?

.....  
 Let  $x$  be the number of kilomoles of air in excess of that required by stoichiometry. The heat removal equation becomes,

$$27.2 = (37,000 \times 335.8 \times 10^{-9} + 29,000 \times 671.6 \times 10^{-9} + 29,000x) \times 80.$$

from which,  $x = 10.6 \times 10^{-6}$  kmole/s.

The ratio of this flow to the stoichiometric flow is

$$R = \frac{10.6 \times 10^{-6}}{839.5 \times 10^{-9}} = 12.6.$$

To keep the temperature rise down to 80 K, the airflow must be increased 13-fold.

This is an excessive flow of air. much more than what is used in practice.

---

## Solution of Problem 9.23

**Prob 9.24** The EV1 was an exceedingly well designed automobile, having excellent aerodynamics and, all over, low losses. With an energy supply of 14 kWh, it had range of over 100 km. It's 100 kW motor allowed very good acceleration making it a "sexy" machine. The problem was that, no matter how good a battery it used, it took a long time to recharge it. If instead of a battery, it had used fuel cells, then *refueling* would take only minutes versus hours for *recharging*.

Imagine that you want to replace the NiMH batteries by a fuel cell battery which, of course, must supply 100 kW of power. The  $V$ - $I$  characteristic of the available Hydrogen/Oxygen fuel cell operating at RTP is

$$V_l = 1.1 - 550 \times 10^{-6} I.$$

The maximum internal heat dissipation capability is 300 W. Product water exits the cell in vapor form.

The fuels cells deliver their energy to a power conditioning unit (inverter) that changes its dc input into ac power The efficiency of this unit can be taken as 100%.

- 
- a. What is the input voltage of the power conditioning unit, in other words, what is the voltage that the fuel cell battery (at 100 kW), must deliver assuming the the smallest possible number of individual cells are used.
- 

.....  
The maximum heat power,  $P_{heat}$ , that each cell can dissipate is 300 W.

$$P_{heat} = P_{in} - P_L. \quad (1)$$

If the current though the cell is  $I$ , then the hydrogen consumption rate (per cell) is

$$\dot{N}_{H_2} = \frac{I}{2qN_0} = \frac{I}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 5.19 \times 10^{-9} I, \quad (2)$$

and

$$P_{in} = |\Delta \bar{h}| \dot{N}_{H_2} = 241.8 \times 10^6 \times 5.19 \times 10^{-9} = 1.255 I. \quad (3)$$

$$P_L = IV_L = I \times (1.1 - 550 \times 10^{-6} I) = 1.1 I - 550 \times 10^{-6} I^2. \quad (4)$$

Introducing Equations 3 and 4 into Equation 1,

$$P_{heat} = 1.255 I - (1.1 I - 550 \times 10^{-6} I^2) = 0.155 I + 550 \times 10^{-6} I^2 = 300. \quad (5)$$

## Solution of Problem 9.24

$$550 \times 10^{-6} I^2 + 0.155 I - 300 = 0. \quad (6)$$

$$\begin{aligned} I &= \frac{-0.155 \pm \sqrt{0.155^2 + 4 \times 550 \times 10^{-6} \times 300}}{2 \times 550 \times 10^{-6}} \\ &= \frac{-0.155 \pm 0.827}{1.10 \times 10^{-3}} = 611.0 \quad \text{A.} \end{aligned} \quad (7)$$

This is the maximum current the cell can deliver without exceeding the 300 W heat dissipation limit.

The load voltage, when this current is flowing is

$$V_L = 1.1 - 550 \times 10^{-6} \times 611 = 0.764 \quad \text{V}, \quad (8)$$

and the power delivered to the load is

$$P_L = V_L I = 0.764 \times 611 = 466.8 \quad \text{W}. \quad (9)$$

To produce 100 kW, about 214 cells will be needed. Such a battery will generate  $214 \times 0.764 = 163.7 \text{ V}$  when connected in series.

The fuel cell battery must deliver 164 V to the inverter.

- b. The 100 kW power are needed only for acceleration. For cruising at 110 km/h, only 20 kW are required. †**  
**How many kg of hydrogen are needed to provide a range of 800 km to the car (using 20 kW)?**

.....  
 If the battery of 214 fuel cells is to deliver 20 kW, then each cell must deliver  $20,000/214 = 93.5 \text{ W}$ .

$$P_L = IV_L = 1.1I - 550 \times 10^{-6} I^2 = 93.5. \quad (10)$$

$$-550 \times 10^{-6} I^2 + 1.1I - 93.5 = 0 \quad (11)$$

$$I = \frac{-1.1 \pm \sqrt{1.1^2 - 4 \times 550 \times 10^{-6} \times 93.5}}{2 \times (-550 \times 10^{-6})} \quad (12)$$

$$I = \frac{-1.1 \pm 1.002}{-110 \times 10^{-6}} = \begin{cases} 89 & \text{A} \\ 1911 & \text{A} \end{cases} \quad (13)$$

Clearly, 1911 A will overheat the cell. The correct current is 89 A which causes the cell voltage to be 1.051 and the battery voltage 225 V.

---

† Just a wild guess!

## Solution of Problem 9.24



A current of 89 A corresponds to a hydrogen consumption rate of

$$\dot{N}_{H_2} = \frac{I}{2qN_0} = \frac{89}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 462 \times 10^{-9} \text{ kmol}(\text{H}_2)/\text{s}, \quad (14)$$

per cell or  $462 \times 214 = 99 \times 10^{-6}$  kmol( $\text{H}_2$ )/s. or  $198 \times 10^{-6}$  kg( $\text{H}_2$ )/s.

It takes 7.27 hours or 26,180 seconds to cover 800 km at 110, km/h. During this time, the amount of hydrogen used up is  $26,180 \times 198 \times 10^{-6} = 5.18$  kg.

5.2 kg of hydrogen

**c. If the hydrogen is stored at 500 atmospheres, how much volume does it occupy at 298 K?**

.....  
5.2 kg correspond to  $\mu = 2.6$  kmol.

$$V = \mu \frac{RT}{p} = 2.6 \frac{8314 \times 298}{500 \times 10^5} = 0.129 \text{ m}^3.$$

129 liters of hydrogen, at 500 atmospheres are needed.

Aluminum canisters of modern design, reinforced by a wrapping of carbon fibers, can store hydrogen at 500 atmospheres. Such canisters can hold 6 kg of  $\text{H}_2$  (860 MJ) and masses less than 90 kg. The size is 1 m in length and 45 cm in diameter.

## Solution of Problem 9.24

**Prob 9.25** A single chamber low-operating-temperature solid oxide fuel cell somewhat similar to the one described by Hibino et al., when operated at a current density of  $6000 \text{ A/m}^2$ , delivers a load voltage that depends on the thickness of the electrolyte in the manner indicated in the table below:

Electrolyte thickness mm	Load Voltage V
0.15	0.616
0.35	0.328
0.50	0.112

This type of cell has essentially straight  $V - I$  characteristics. The specific resistance,  $\mathfrak{R}$ , of the cell (see 9.8.3.1) can be considered as consisting of two components,  $\mathfrak{R}_1 + \mathfrak{R}_2$ , where  $\mathfrak{R}_1$  is the resistance of the electrolyte and  $\mathfrak{R}_2$  represents all other resistances of the cell. The open-circuit voltage is  $0.892 \text{ V}$ .

- a. If it were possible to use a vanishingly thin electrolyte, what maximum power would the cell be able to deliver?

.....  
Since the cell has essentially straight  $V - I$  characteristics, the load voltage is

$$V = V_{oc} - \mathfrak{R}J,$$

where  $\mathfrak{R} \equiv \mathfrak{R}_1 + \mathfrak{R}_2$  is the **specific resistance of the cell**.

Plausibly, the electrolyte resistance is proportional to its thickness,  $d$ , so,  $\mathfrak{R}_1 \equiv \rho d$ , where  $\rho$  is a proportionality constant with the dimensions of  $\Omega\text{m}$ .

Now,

$$V = V_{oc} - (\rho d + \mathfrak{R}_2)J,$$

from which

$$\rho d + \mathfrak{R}_2 = \frac{V_{oc} - V}{J}.$$

Using the available data,

$$\begin{cases} 0.15 \times 10^{-3} \rho + \mathfrak{R}_2 = \frac{0.892 - 0.616}{6000} = 4.60 \times 10^{-5} \\ 0.35 \times 10^{-3} \rho + \mathfrak{R}_2 = \frac{0.892 - 0.328}{6000} = 9.40 \times 10^{-5} \\ 0.50 \times 10^{-3} \rho + \mathfrak{R}_2 = \frac{0.892 - 0.112}{6000} = 13.0 \times 10^{-5} \end{cases}$$

Using the first and third equations above, we obtain,

$$\rho = 0.240 \Omega\text{m},$$

$$\mathfrak{R}_2 = 1.00 \times 10^{-5} \Omega\text{m}^2.$$

## Solution of Problem 9.25

For infinitely thin electrolytes ( $d = 0$ ),  $\Re = \Re_2$ , and

$$V = 0.892 - 1.00 \times 10^{-5} J.$$

The power density delivered to the load is

$$P_L = 0.892J - 1.00 \times 10^{-5} J^2,$$

which has a maximum when

$$0.892 - 2 \times 1.00 \times 10^{-5} J = 0, \quad \text{or} \quad J = 44,600 \quad \text{A/m}^2$$

At this current, the load voltage will be

$$V = 0.892 - 10^{-5} \times 44,600 = 0.446 \quad \text{V}.$$

Of course, the load voltage will be half of the open-circuit voltage because, for maximum power, the load resistance,  $R_L$ , must be equal to the internal resistance.

The power output is

$$P_L = V_L J = 0.446 \times 44,600 = 19,900 \quad \text{W/m}^2.$$

The power output is 20 kW/m<sup>2</sup>.

**b. What would be the corresponding load resistance if the cell has an effective electrode area of 10 by 10 cm?**

.....  
In a 10 by 10 cm cell, the current, at maximum power, will be

$$I = AJ = 0.01 \times 44,600 = 446 \quad \text{A}.$$

The load resistance must be

$$R_L = \frac{V_L}{I_L} = \frac{0.446}{446} = 0.001 \quad \Omega.$$

The load resistance must be 1 milliohm.

**c. Compare the power output of the cell with that for the cell with 0.15 mm-thick electrolyte.**

.....  
**Solution of Problem 9.25**

The cell with 0.15 mm-thick electrolyte has a specific (electrolyte) resistance of

$$\mathfrak{R}_1 = \rho d = 0.24 \times 0.15 \times 10^{-3} = 36 \times 10^{-6} \quad \Omega\text{m}^2,$$

and a total specific resistance of

$$\mathfrak{R} = \mathfrak{R}_1 + \mathfrak{R}_2 = 36 \times 10 \times 10^{-6} + 10 \times 10^{-6} = 46 \times 10^{-6} \quad \Omega\text{m}^2.$$

The specific resistance is  $46 \mu\Omega\text{m}^2$  and this must also be the resistance of the load. The current, in this case will be  $I = 0.446/46 \times 10^{-6} = 9,700 \text{ A/m}^2$  and the power output is

$$P_L = 0.446 \times 9700 = 4,300 \quad \text{W/m}^2.$$

The power output is 4.3 kW per  $\text{m}^2$  of active area.

It can be seen that the maximum power output from the cell increases rapidly as the electrolyte becomes thinner. This suggests the use of extremely thin electrolytes, perhaps supported by the electrodes.

---

## Solution of Problem 9.25

**Prob 9.26** Solid Oxide fuel cells manufactured by Siemens Westinghouse have a very pronounced curvature in their  $V$ - $J$  characteristics. One class of cells using “ribbed” units behave according to

$$V_L = 0.781 - 1.607 \times 10^{-6} J - 6.607 \times 10^{-9} J^2,$$

where  $J$  is the current density in A/m<sup>2</sup> and  $V_L$  is the load voltage in V.

a. What is the open-circuit voltage of the cell?

The open circuit of the cell is 0.781 V.

b. What is the voltage of the cell when delivering maximum power to a load?

.....

$$\begin{aligned} P_L &= 0.781J - 1.607 \times 10^{-6} J^2 - 6.607 \times 10^{-9} J^3, \\ \frac{dP_L}{dJ} &= 0.781 - 3.214 \times 10^{-6} J - 19.82 \times 10^{-9} J^2 = 0, \\ J &= \frac{-3.214 \times 10^{-6} \pm \sqrt{(3.214 \times 10^{-6})^2 + 4 \times 19.82 \times 10^{-9} \times 0.781}}{-2 \times 19.82 \times 10^{-9}} \\ &= \frac{3.24 \times 10^{-6} \pm 248.9 \times 10^{-6}}{-39.64 \times 10^{-9}}, = \begin{cases} -6360 & \text{A/m}^2. \\ 6197 & \text{A/m}^2 \end{cases} \end{aligned}$$

Clearly, only the positive solution is valid. The negative solution corresponds to operating the device as an electrolyzer.

Using the positive solution,

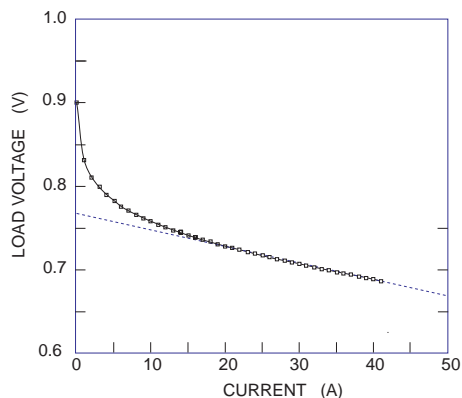
$$V_L = 0.781 - 1.607 \times 10^{-6} \times 6197 - 6.607 \times 10^{-9} \times 6197^2 = 518 \quad \text{V.}$$

The load voltage is 0.518 V.

## Solution of Problem 9.26

**Prob 9.27** The  $V$ - $I$  characteristics of a given fuel cell (measured with incredible precision) are tabulate as shown. See plot. The measurements were made at RTP. Water leaves the cell as a gas.

Load Current (A)	Load Voltage (V)	Load Current (A)	Load Voltage (V)
0.00	0.90000		
0.5	0.84919		
1.00	0.83113	21.00	0.72622
2.00	0.81144	22.00	0.72390
3.00	0.79922	23.00	0.72163
4.00	0.79018	24.00	0.71942
5.00	0.78291	25.00	0.71725
6.00	0.77677	26.00	0.71514
7.00	0.77142	27.00	0.71306
8.00	0.76664	28.00	0.71103
9.00	0.76230	29.00	0.70902
10.00	0.75831	30.00	0.70706
11.00	0.75461	31.00	0.70512
12.00	0.75114	32.00	0.70322
13.00	0.74786	33.00	0.70134
14.00	0.74476	34.00	0.69949
15.00	0.74180	35.00	0.69766
16.00	0.73896	36.00	0.69586
17.00	0.73624	37.00	0.69408
18.00	0.73361	38.00	0.69232
19.00	0.73107	39.00	0.69058
20.00	0.72861	40.00	0.68886
		41.00	0.68715



**a. Calculate the efficiency of the cell when 10 A are being delivered.**

.....  
When  $I_L = 10$  A,  $V_L = 0.75831$  V as indicated in the tabulated data. This means that

$$P_L = 10 \times 0.75831 = 7.583 \quad \text{W.} \quad (1)$$

At the prescribed current, the rate of hydrogen use is

$$\begin{aligned} \dot{N} &= \frac{I_L}{2qN_0} = \frac{10}{2 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{26}} \\ &= 51.89 \times 10^{-9} \quad \text{kmoles(H)/s.} \end{aligned} \quad (2)$$

Thus, the input power is

$$P_{in} = \dot{N} \Delta h_f^\circ = 51.89 \times 10^{-9} \times 241.8 \times 10^6 = 12.548 \quad \text{W.} \quad (3)$$

## Solution of Problem 9.27

Consequently, the efficiency is

$$\eta = \frac{P_L}{P_{in}} = \frac{7.583}{12.548} = 0.604. \quad (4)$$

The efficiency is 60.4%

- b. Calculate the rate of heat production by the cell when the load current,  $I_L$  is 10 A.**

$$P_{heat} = P_{in} - P_L = 12.548 - 7.583 = 4.965 \quad \text{W.} \quad (5)$$

The rate of heat production is 4.96 W.

- c. Visually, the characteristics appear as a straight line for sufficiently large current. This suggests that, in the relatively large current region, one can use the equation**

$$V_L = V_{oc} - R_{app}I,$$

where  $R_{app}$  is the apparent internal resistance of the cell as inferred from the straight line. Estimate the value of  $R_{app}$  using

**c.1 using the region  $30 \leq I \leq 41$  A.**

**c.2 using the region  $10 \leq I \leq 41$  A.**

$I_1$ (A)	$I_2$ (A)	$ \Delta I $ (A)	$V_1$ (V)	$V_2$ (V)	$ \Delta V $ (V)	$R_{app}$ (m $\Omega$ )
30	41	11	0.70706	0.68715	0.01991	1.810
10	41	31	0.75831	0.68715	0.07116	2.295

The apparent resistance depends on the current interval chosen.

For the interval 30 to 41 A, the apparent resistance is 1.81 m $\Omega$   
 For the interval 10 to 41 A, the apparent resistance is 2.30 m $\Omega$

These values do not accurately correspond to  $R_{int}$  because this cell has considerable activation voltage that also contributes to the slope.

- d. For each of the values of  $R_{app}$ , above, determine the magnitude of the various sources of heat (Joule effect, etc.) when the cell delivers 10 A to the load. Clearly, because you used a straight-line approximation, the activation voltage does not contribute to the heat calculation.**

## Solution of Problem 9.27

Since one of the sources of heat is the open-circuit voltage drop, it is necessary to calculate  $V_{oc}$  for the two characteristics. We must extrapolate the straight line and find its intercept of the  $I = 0$  axis. We will use

$$V_{oc} = V_L + R_{app}I. \quad (6)$$

Using  $V_L = 0.68715$  V and the corresponding  $I = 41$  A,

$$\begin{cases} V_{oc} = 0.68715 + 0.001810 \times 41 = 0.76136 & \text{V,} \\ V_{oc} = 0.68715 + 0.002295 \times 41 = 0.78124 & \text{V.} \end{cases}$$

Thus, for these two cases,  $P_{oc} = I(V_{rev} - V_{oc})$ ,

$$\begin{cases} P_{oc} = 10 \times (1.185 - 0.76136) = 4.236 & \text{W,} \\ P_{oc} = 10 \times (1.185 - 0.78124) = 4.038 & \text{W.} \end{cases}$$

The Joule losses are  $P_{jpoule} = R_{app}I^2$ ,

$$\begin{cases} P_{joule} = 0.001810 \times 10^2 = 0.182 & \text{W,} \\ P_{joule} = 0.002295 \times 10^2 = 0.230 & \text{W,} \end{cases}$$

The thermodynamic heat is the same for the two cases and is

$$P_{thermodynamic} = \dot{N} \times T|\Delta S| = 51.89 \times 10^{-9} \times 13.24 \times 10^6 = 0.687 \quad \text{W.}$$

The calculated heat production rate for the two cases is

$$\begin{cases} P_{heat} = 4.236 + 0.182 + 0.687 = 5.11 & \text{W,} \\ P_{heat} = 4.038 + 0.230 + 0.687 = 4.96 & \text{W.} \end{cases}$$

This compares with the value of 4.96 W calculated in Question 2.

The results from the simplified (straight-line) approach are reasonably close to the correct value especially in the case of the apparent resistance obtained from the wider current range.

- e. Now determine accurately the value of the internal resistance,  $R_{int}$ , i.e., include the activation voltage in the  $V_I$  characteristics.**

.....  
The applicable formula relating  $V_L$  to  $I_L$  is

$$V_L = V_{oc} - R_{int}I_L - V_2 \ln \frac{I_L}{I_0}. \quad (7)$$

The slope is

$$\frac{V_L}{dI_L} = -R_{int} - \frac{V_2}{I_L}. \quad (8)$$

The value of  $dV_L/dI_L$  can be found from the data in the table. Since there are two unknowns in Equation 8, ( $R_{int}$  and  $V_2$ ), we have to pick two different currents. Let us use 30 A and 40 A, to which

## Solution of Problem 9.27



the corresponding slopes are  $(0.70512 - 0.70902)/2 = -0.001950 \, \Omega$  and  $(0.68715 - 0.69058)/2 = -0.001715 \, \Omega$ .

We can now set up a pair of simultaneous equations:

$$\begin{cases} -0.001950 = -R_{int} - \frac{V_2}{30}, \\ -0.001715 = -R_{int} - \frac{V_2}{40}. \end{cases}$$

leading to

$$V_2 = 0.0282 \quad \text{V},$$

and

$$R_{int} = 0.00101 \quad \Omega.$$

Observe that the 1.01 milliohms value of  $R_{int}$  is, as expected, substantially smaller than the estimated values of around 2 milliohms for  $R_{app}$ .

If we had picked lower current values, say 10 A and 20 A, we would have found

$$V_2 = 0.0286 \quad \text{V},$$

and

$$R_{int} = 0.001005 \quad \Omega.$$

The internal resistance of the cell is 1 milliohm.

**f. Finally, write a set of equations describing the manner in which the load voltage depends on the load current. Check the values obtained from your equations against the tabulated data. Do this for  $I_L = 40 \, \text{A}$  and for  $I_L = 0.5 \, \text{A}$ .**

$V_{oc} = 0.90000 \, \text{V}$  (from the tabulated data).

By using any value of  $I_L$  and the corresponding value of  $V_L$ , and applying these values to Equation 7, we can solve for  $I_0$ . Say,  $I_L = 40 \, \text{A}$  and  $V_L = 0.6886 \, \text{V}$ ,

$$0.6886 = 0.90000 - 0.00101 \times 40 - 0.0282 \ln \frac{40}{I_0} \quad (9)$$

$$\ln \frac{40}{I_0} = \frac{-0.6886 + 0.90000 - 0.00101 \times 40}{0.0282} = 6.055, \quad (10)$$

$$I_0 = 0.09388 \quad \text{A}.$$

The characteristics are

$$V_L = 0.90000 - 0.00101 I_L - 0.0282 \ln \frac{I_L}{0.09388}$$

Introducing  $I_L = 40 \, \text{A}$  in the above equation, one obtains, of course,  $V_L = 0.6886 \, \text{V}$ , exactly the observed voltage

On the other hand, introducing  $I_L = 0.5 \, \text{A}$ , one obtains,  $V_L = 0.85233 \, \text{V}$ , somewhat larger than the observed value of  $0.84919 \, \text{V}$ .

## Solution of Problem 9.27

**g. Explain why your equation overestimates  $V_L$  at small currents.**

.....  
 The small discrepancy in the value of  $V_L$  for 0.5 A would grow to intolerable values as  $I_L \rightarrow 0$ , owing to the logarithm in the equation. It is possible to write a pair of equations that reproduce the tabulated data. After all, that is how the data were generated. Here is the cumbersome procedure:

Choose two values of  $I_L$ . Say, 20 A and 40 A.

From  $V_{act} = V_{oc} - R_{int}I_L - V_L$ , calculate the corresponding values of  $V_{act}$ . Remember that  $R_{int} = 0.001 \Omega$ ,  $V_{oc} = 0.90$ , and  $V_L$  corresponding to each  $I_L$  can be read from the tabulation. This yields 2 values for  $V_{act}$ : 0.1514 V and 0.1711 V.

For large values of  $I_L$ ,

$$I_L = I_0 \exp\left(\alpha \frac{q}{kT} V_{act}\right),$$

which, for  $T = 298$  K, yields

$$\begin{aligned} I_0 &= \frac{I_L}{\exp(\alpha V_{act}/0.0257)} \\ I_0 &= \frac{20}{\exp(\alpha \times 0.1514/0.0257)} \\ I_0 &= \frac{40}{\exp(\alpha \times 0.1711/0.0257)} \\ \frac{20}{\exp(\alpha \times 0.1514/0.0257)} &= \frac{40}{\exp(\alpha \times 0.1711/0.0257)} \end{aligned}$$

from which,  $\alpha = 0.904$ .

$$I_0 = \frac{20}{\exp(0.904 \times 0.1514/0.0257)} = 0.0971.$$

We can now write a full expression for  $I_L$  as a function of  $V_{act}$ . See text.

$$I_L = 0.0971 [\exp(35.187V_{act}) - \exp(-3.724V_{act})] \quad (11)$$

$$V_L = 0.9 - 0.001I_L - V_{act}. \quad (12)$$

Select a range of plausible values for  $V_{act}$ . For each, calculate  $I_L$  using Equation 11. With the values of  $V_{act}$  and  $I_L$ , calculate the corresponding  $V_L$ . In this manner, we can reconstruct a table of  $I_L$  versus  $V_L$  which is fairly accurate all the way down to  $I_L = 0$ .

---

## Solution of Problem 9.27

**Prob 9.28** Although low voltage automotive batteries have been standardized at 12 V, no such standards have been agreed for automotive traction batteries. Some hybrid cars use 275 V motors and 275 V batteries (some use 550 V motors powered by 275 V batteries.)

Consider a fuel cell battery rated 100 kW at 275 V. It uses pure hydrogen and pure oxygen, both at 1 atmosphere pressure. The battery, consisting of 350 cells, operates at 390 K. To simplify the problem, assume 298 K thermodynamics.

Assume a linear  $V$  vs  $I$  characteristic for the fuel cells.

- a. What is the hydrogen consumption (in kg of  $H_2$  per hour) when the battery delivers 100 kW?

.....  
The current through each cell is the same as that through the battery:

$$I = \frac{100,000}{275} = 363.6 \text{ A.} \quad (1)$$

Thus, each cell consumes,

$$\begin{aligned} \dot{N} &= \frac{I}{n_e q N_0} = \frac{363.6}{2 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{26}} = 1.887 \times 10^{-6} \text{ kmole/s} \\ &= 0.01359 \text{ kg/hr.} \end{aligned} \quad (2)$$

Since there are 350 cells, the consumption is  $350 \times 0.01359 = 4.755$  kg/hr.

Hydrogen consumption: 4.76 kg/hr.

- 
- b. The retarding force on a car can be represented by a power series in  $U$  (the velocity of the car):

$$F = a_0 + a_1 U + a_2 U^2. \quad (3)$$

$a_1 U$  represents mostly the force associated with deformation of tires.  $a_2 U^2$  is the aerodynamic retarding force and is

$$a_2 = \frac{1}{2} \rho C_D A U^2 \quad (4)$$

where  $\rho = 1.29 \text{ kg/m}^3$  is the density of air,  $C_D = 0.2$  is the drag coefficient, and  $A = 2 \text{ m}^2$ , is the frontal area of the vehicle. Make  $a_0 = 0$ .

When delivering 50 kW, the battery voltage is 295 V. When cruising at a constant, moderate—speed of 80 km/hr—the car uses only 15 kW. What is the range of the car under such conditions if the hydrogen tank can store 4 kg of the gas? This assumes flat, horizontal roads and no wind.

.....  
Using the values given,

$$F = a_1 U + 0.2580 U^2. \quad (5)$$

## Solution of Problem 9.28

The current drawn when 50 kW are delivered is

$$I = \frac{50,000}{295} = 169.5A. \quad (6)$$

We now use the load voltage equation,

$$V_L = V_{OC} - I R_{int}. \quad (7)$$

$$\begin{cases} 275 = V_{OC} - 363.6R_{int}, \\ 295 = V_{OC} - 169.5R_{int}. \end{cases}$$

This yields

$$V_L = 312.5 - 0.103I. \quad (8)$$

The current at 15 kW is

$$I = \frac{15,000}{V_L} = \frac{15,000}{312.5 - 0.103I} \quad (9)$$

This quadratic equation yields two values for I, the lower of which is

$$I = 48.78 \quad A. \quad (10)$$

Each cell now consumes,

$$\begin{aligned} \dot{N} &= \frac{I}{n_e q N_0} = \frac{48.78}{2 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{26}} = 253.1 \times 10^{-9} \quad \text{kmole/s} \\ &= 506.3 \times 10^{-9}, \quad \text{kg/s} \end{aligned} \quad (11)$$

and the battery uses  $350 \times 506.3 \times 10^{-9} = 177.2 \times 10^{-6} \quad \text{kg/s}$

The endurance of the car is

$$T = \frac{4}{\dot{N}} \quad \text{seconds}. \quad (12)$$

In the above formula,  $\dot{N}$  is in kg/s.

The range is

$$D = UT = 4 \frac{U}{\dot{N}} \quad \text{meters}. \quad (13)$$

80 km/hr correspond to 22.22 m/s, hence, the car covers a distance of

$$D = 22.22 \frac{4}{177.3 \times 10^{-6}} = 501,600 \quad \text{m} \quad (14)$$

The car can travel just over 500 km on one full tank.

### c. How slow must the car drive to do 1000 km on 4 kg of H<sub>2</sub>?

The power necessary to overcome the drag forces on the car is

$$P = FU = a_1 U^2 + 0.2580 U^3 \quad (15)$$

We must find  $a_1$ .

## Solution of Problem 9.28

At 22.22 m/s it takes 15 kW to drive the car:

$$15,000 = 22.22^2 a_1 + 0.258 \times 22.22^3, \quad (16)$$

from which,

$$a_1 = 24.65 \quad (17)$$

Consequently, at any speed, the power to drive the car is

$$P = 24.65U^2 + 0.258U^3. \quad (18)$$

This power must come from the fuel cell battery:

$$P = 312.5I - 0.103I^2. \quad (19)$$

and we have,

$$24.65U^2 + 0.258U^3 = 312.5I - 0.103I^2 \quad (20)$$

Solving for  $I$  as a function of  $U$ ,

$$I = 1517 - \sqrt{2.301 \times 10^6 - 239.3U^2 - 2.505U^3} \quad (21)$$

This yields the current required to drive the car at any given velocity,  $U$ .

From Equation 13,

$$\frac{U}{\dot{N}} = \frac{D}{4} = \frac{1,000,000}{4} = 250,000, \quad (22)$$

where  $\dot{N}$  is the fuel consumption of the whole battery in kg/s not kmol/s.

$$\dot{N} = \frac{350I}{qN_0} \quad \text{kg(H}_2\text{) per sec.} \quad (23)$$

$$\frac{U}{I} = \frac{350 \times 250,000}{qN_0} = 0.9081. \quad (24)$$

Introducing the value of  $I$  from Equation 21,

$$\frac{U}{1517 - \sqrt{2.301 \times 10^6 - 239.3U^2 - 2.505U^3}} = 0.9081 \quad (25)$$

The above equation has three solutions:

$$\begin{cases} U = -108.3 \text{ m/s} \\ U = 0.087 \text{ m/s} \\ U = 12.23 \text{ m/s} \end{cases}$$

Of the two positive roots, the larger one is the one that makes most sense,

To drive 1000 km you must slow down to 12.2 m/s or 44.0 km/h.

## Solution of Problem 9.28

**Prob 9.29** To test a fuel cell in a laboratory, an ac voltage generator (peak-to-peak voltage  $v_{pp} = 0.001$  V) was connected in series with the load and an ac ammeter (peak-to-peak current  $i_{pp}$ ) was used to measure the load current fluctuations caused by the varying  $V_L$ . The frequency used was low enough to cause any reactive component in the measurement to be negligible. The following measurements were obtained:

$I_L$ A	$V_L$ V	$i_{pp}$ A
5.34	0.956	0.186
10.67	0.936	0.366

It was observed that there was a  $180^\circ$  phase relationship between  $v_{pp}$  and  $i_{pp}$ —that is, that increasing the voltage, actually reduced the current. Calculate the true internal resistance of the cell.

The  $I$  vs  $V$  characteristic of a fuel cell can be represented mathematically by

$$V_L = V_{OC} - R_{int}I - V_{act}, \quad (1)$$

A good approximation for the dependence of  $V_{act}$  on  $I$  (unless  $I$  is very small) is

$$V_{act} = V_2 \ln \frac{I}{I_0}. \quad (2)$$

In this case,

$$V_L = V_{OC} - R_{int}I - V_2 \ln \frac{I}{I_0}. \quad (3)$$

$$\frac{V_L}{dI} = -R_{int} - \frac{V_2}{I}. \quad (4)$$

From the table of observed values, one can calculate  $dV_L/dI = 0.001/i_{pp}$ :

$I_L$ A	$V_L$ V	$i_{pp}$ A	$dV_L/dI$ V/A
5.34	0.956	0.186	-0.005376
10.67	0.936	0.366	-0.002732

We can now set-up a pair of simultaneous equations,

$$\begin{cases} -0.005376 = -R_{int} - \frac{V_2}{5.34}, \\ -0.002732 = -R_{int} - \frac{V_2}{10.67}. \end{cases} \quad (5)$$

which yield

$$R_{int} = 0.000083 \quad \Omega \quad \text{and} \quad V_2 = 0.0283 \quad \text{V}.$$

The true internal resistance of the cell is 83 microohms

## Solution of Problem 9.29

**Prob 9.30 Hydrogen-oxygen fuel cell.** Although the temperature of the cell will vary throughout its operation, use thermodynamic data for RTP so as not to complicate the computation.

Each cell is 3 mm thick and has a total area of 10 by 10 cm.

The density of each cell is equal to twice the density of water, and the specific heat capacity of the cell is 10% of the specific heat of water. This means that it takes 24 J of heat to raise the cell temperature by 1 kelvin.

Under all circumstances, the product water is removed from the cell in vapor form.

The highest allowable operating temperature of the cell is 450 K.

Although heat is removed from the cell by several different mechanisms, the net effect is that the rate of heat removal is proportional to  $T - 300$ : In fact the heat removal rate,  $\dot{Q}_{rem} = 0.3(T - 300)$  W.

Laboratory tests reveal that when the load current is 2 A, the load voltage is 0.950 V, and when the load current is 20 A, the load voltage falls to 0.850 V.

- a. Write an equation relating  $V_L$  to  $I_L$ , assuming a linear relationship between these variables.

.....  
The negative of the slope of the  $V$ - $I$  characteristics is the apparent resistance,  $R_{app}$ ,

$$R_{app} = -\frac{\Delta V_L}{\Delta I_L} = -\frac{0.85 - 0.95}{20 - 2} = 0.00555 \quad \Omega. \quad (1)$$

The load voltage is to be a linear function of the load current:

$$V_L = V_{oc} - R_{app}I_L. \quad (2)$$

Take  $I_L = 20$  A. The corresponding  $V_L$  is 0.85 V,

$$0.85 = V_{oc} - 0.00555 \times 20, \quad (3)$$

$$V_{oc} = 0.85 + 0.00555 \times 20 = 0.961 \quad \text{V}. \quad (4)$$

$$V_L = 0.961 - 0.00555I_L.$$

- 
- b. What is the maximum power the cell can deliver?

.....  
The power delivered to the load is

$$P_L = V_L I_L = 0.961I_L - 0.00555I_L^2. \quad (5)$$

## Solution of Problem 9.30

$$\frac{dP_L}{dI_L} = 0.961 - 0.0111I_L = 0, \quad (6)$$

$$I_{L_{max}} = 86.6 \quad \text{A}. \quad (7)$$

$$P_{L_{max}} = 0.961 \times 86.6 - 0.00555 \times 86.6^2 = 41.6 \quad \text{W}. \quad (8)$$

The maximum power the cell can deliver is 41.6 W.

**c. Show that this maximum power cannot be delivered continuously because it would cause the cell temperature to exceed the maximum allowable operating temperature.**

.....  
To deliver a current of 86.6 A, the cell must consume hydrogen at a rate of

$$\dot{N} = \frac{I_L}{n_e q N_0} = \frac{86.6}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 450 \times 10^{-9} \quad \text{kmole}(\text{H}_2)/\text{s}. \quad (9)$$

Consequently, the input power to the cell is,

$$P_{in} = \dot{N} \Delta \bar{h}_f = 450 \times 10^{-9} \times 241.8 \times 10^6 = 108.8 \quad \text{W}. \quad (10)$$

The amount of heat power generated by the cell is

$$P_{heat} = P_{in} - P_L = 108.8 - 41.6 = 67.2 \quad \text{W}. \quad (11)$$

To remove this amount of heat, the cell temperature must be

$$Q_{rem} = P_{heat} = 67.2 = 0.3(T - 300), \quad (12)$$

from which,  $T = 524.0 \text{ K}$ .

The cell would operate at 524 K, way above the maximum allowable operating temperature of 450 K.

**d. What is the maximum power that the cell can deliver continuously to a load?**

.....  
The maximum power is limited by the necessity of not exceeding the maximum allowable operating temperature of 450 K. At this temperature the cell can reject heat at a rate of

$$\dot{Q}_{heat} = 0.3(450 - 300) = 45 \quad \text{W}. \quad (13)$$

## Solution of Problem 9.30



This means that the maximum heat power,  $P_{heat}$  the cell can generate is 45 W.

$$\begin{aligned} P_{heat} &= P_{in} - P_L = \dot{N}|\Delta\overline{h_f}| - (0.961I_L - 0.00555I_L^2) \\ &= \frac{I_L}{n_e q N_0} |\Delta\overline{h_f}| - (0.961I_L - 0.00555I_L^2) \\ 1.255I_L - 0.961I_L + 0.00555I_L^2 &= 0.2938I_L + 0.00555I_L^2 = 45 \quad (14) \end{aligned}$$

We used  $\dot{N}|\Delta\overline{h_f}| = 242.8 \times 10^6$  J/kmole because the product water stays in vapor form. The two roots of this equation are

$$I_L = \begin{cases} 67.4 & \text{A} \\ -120.3 & \text{A.} \end{cases} \quad (15)$$

Only the positive root is valid: the negative root represents a current being driven into the cell.

The acceptable current causes a power,  $P_L$ , to be delivered to the load,

$$P_L = 0.961 \times 67.4 - 0.00555 \times 67.4^2 = 39.6 \quad \text{W.} \quad (16)$$

The cell can deliver at most a sustained power of 39.6 W.

**e. Although the cell cannot deliver maximum power continuously, it can do so for a short time if it starts out cold—that is, if its initial temperature is 300 K. It will generate more heat than it can shed and its temperature will rise. How long can the cell (initially at 300 K) deliver maximum power to the load without exceeding the 450 K temperature limit?**

At maximum power, the cell generates 67.2 W of heat, independently of the temperature. The heat power removed is  $0.3(T - 300)$  W. Hence, heat accumulates at a rate

$$\dot{Q} = 67.2 - 0.3(T - 300) = 157.2 - 0.3T. \quad (17)$$

The heat capacity of the cell is  $c = 24$  J/K. As a consequence, the temperature changes at a rate

$$\frac{dT}{dt} = \frac{\dot{Q}}{c} = \frac{157.2 - 0.3T}{24} = 6.55 - 0.0125T. \quad (18)$$

Separating variables,

$$\frac{dT}{6.55 - 0.0125T} = dt \quad (19)$$

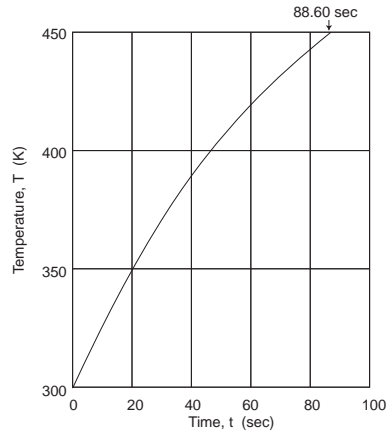
## Solution of Problem 9.30

and integrating from  $T = 300$  K to  $T = 450$  K,

$$\int_{300}^{450} \frac{dT}{6.55 - 0.0125T} = -80 [\ln(6.55 - 0.0125T)] \Big|_{300}^{450} =$$

$$-80 [\ln(6.55 - 0.0125 \times 450) - \ln(6.55 - 0.0125 \times 300)] = 88.61 \text{ s(20)}$$

The graph below shows how the temperature rises with the time elapsed since starting the operation.



## Solution of Problem 9.30

**Prob 9.31** An ideal hydrogen/air fuel cell operates at 298 K. A mixture of hydrogen and water vapor is fed in at 3 atmospheres pressure. Moist air is also fed in at this same pressure. In both the fuel and the oxidant streams, the partial pressure of the water vapor is 0.5 atmosphere. What is the voltage the ideal cell delivers to a 1-ohm load? Please calculate the voltage to a millivolt precision.

.....  
At RTP, an ideal hydrogen/oxygen fuel cell produces a voltage of 1.185 V independently of the load voltage. At different reactant and product gas pressure the voltage will be

$$V = 1.185 + \Delta V, \quad (1)$$

where

$$\Delta V = \frac{RT \ln p_{H_2} + \frac{1}{2} RT \ln p_{O_2}}{2qN_0}.$$

We have to find the partial pressures of hydrogen,  $p_{H_2}$ , and of oxygen,  $p_{O_2}$ .

In the fuel stream, 0.5 atmospheres are water vapor. This leaves a partial pressure of 2.5 atmos for the hydrogen.

The oxidizer stream consists of 2.5 atmospheres of air and 0.5 atmospheres of water vapor. Of the 2.5 atmospheres of air, 20% is oxygen, which, consequently has a partial pressure of  $0.2 \times 2.5 = 0.5$  atmos.

Thus,

$$\Delta V = \frac{8314 \times 298 (\ln 2.5 + \frac{1}{2} \ln 0.5)}{2 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{26}} = 0.0062 \text{ V}. \quad (2)$$

The output voltage rises to 1.191 V.

## Solution of Problem 9.31

**Prob 9.32** A 24-cell hydrogen/air fuel cell battery operating at RTP consists of cells having the characteristics,

$$V_L = 1.05 - 0.001I_L \quad (1)$$

Water is exhausted from the battery as a vapor.

The heat removal system can, at most, remove 5278 W of heat. What is the maximum power the battery can deliver (under steady state conditions) to a load?  
.....

$$P_{in} = \frac{\Delta h f^\circ}{2qN_0} I = \frac{241.8 \times 10^6}{2 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{26}} I = 1.255I \quad (2)$$

$$P_L = 1.05I - 0.001I^2, \quad (3)$$

$$P_{heat} = \frac{5278}{24} = 219.9 = P_{in} - P_L = 1.255I - 1.05I + 0.001I^2 \quad (4)$$

from which

$$0.00I^2 + 0.205I - 219.9 = 0, \quad (5)$$

$$I^2 + 205I - 219,900 = 0, \quad (6)$$

$$I = -205 \pm \sqrt{\frac{205^2 + 4 \times 219,900}{2}} = -102.5 \pm 480 = \begin{cases} -582.5 \text{ A} \\ 377.5 \text{ A} \end{cases} \quad (7)$$

The negative current corresponds to operating the device as an electrolyzer. Thus, only the positive value is acceptable.

Introducing this value into Equation 3,

$$P_L = 253.9 \text{ W}. \quad (8)$$

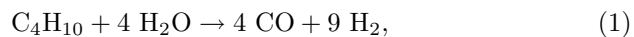
This is per fuel cell. For the 24-cell battery, the power delivered is  $24 \times 253.9 = 6093 \text{ W}$ .

The power delivered to the load is 6093 W.

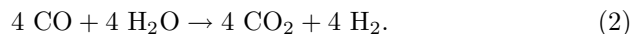
## Solution of Problem 9.32

**Prob 9.33** A domestic fuel cell system in a rural area is to be fed by butane. This gas is to be steam reformed and the resulting carbon monoxide is to be shifted to hydrogen. Assuming no losses, how many kg of hydrogen can be extracted from each kg of butane?

.....  
The empirical formula for butane is  $C_4H_{10}$ . When steam reformed.



and when the 4 kmoles of carbon monoxide are shifted,



The overall reaction is



Since the molecular mass of butane is 58 and that of  $H_2$  is 2, we see that 58 kg of butane are transformed into 26 kg of hydrogen, a yield of 0.448.

1 kg of butane yields 0.45 kg of hydrogen.
--

---

Solution of Problem    9.33

**Prob 9.34** A hydrogen/oxygen fuel cell operating at 298 K is fed (on the anode side) a mixture of hydrogen and water vapor—for each kg of hydrogen there are 1.8 kg of water vapor. The total pressure of the mixture is 3 atmospheres.

On the cathode side, it is fed moist air also at 3 atmospheres—for each kg of air there are 0.125 kg of water. Assume that air consists of 20% oxygen and 80% nitrogen, by volume.

The product is liquid water (remember to use a  $\Delta G_f^\circ$  of  $-237.2$  MJ/kmole, not  $-228.6$ ).

The characteristics of the fuel cell are given below:

- The open-circuit voltage,  $V_{oc}$ , is 139 mV lower than the reversible voltage ( $V_{rev}$ ) owing to unavoidable unwanted side reactions, mostly at the cathode.
- The internal resistance,  $R_{int}$ , of the cell is 5.1 m $\Omega$ .
- The exchange currents add up to  $I_0 = 0.60$  A.
- The transfer coefficient,  $\alpha$ , is 0.7.

Transport losses are negligible in the region of operation.

**a - What is the reversible voltage of this cell? Please show 4 significant figures.**

Remember that the liquid water that results from the hydrogen/oxygen reaction is incompressible, hence the pressure of the product plays no role. However, the free energy of the reaction is influenced by the partial pressure of hydrogen,  $p_{H_2}$ , and of the oxygen,  $p_{O_2}$ . We must determine these pressures.

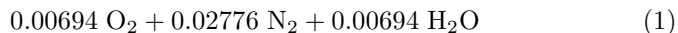
#### Fuel

A 1:1.8 mixture, by mass, of hydrogen and water vapor corresponds to a kilomolar ratio of  $1/2 : 1.8/18$  or 1 kilomole of hydrogen for 0.2 kmoles of water, for a total of 1.2 kilomols. Since the pressures are proportional to the number of kilomols of gas, we have a total pressure of  $1.2\lambda = 3$  atmospheres, where  $\lambda$  is a proportionality constant. From this,  $\lambda$  is 2.5. Hence the partial pressure of hydrogen is  $p_{H_2} = 1 \times 2.5 = 2.5$  atmospheres. Incidentally, that of the water vapor is 0.5 atmospheres.

#### Oxidizer

Assuming that air consists of 20% oxygen (molecular mass 32 daltons) and 80% nitrogen (molecular mass 28 daltons), by volume, the mean molecular mass of air is  $0.2 \times 32 + 0.8 \times 28 = 28.8$  daltons. 1 kg of air corresponds  $1/28.8 = 0.0347$  kmoles of which 0.00694 kilomoles are oxygen and 0.02776 kilomoles are nitrogen. 0.125 kg of water vapor correspond to 0.00694 kmoles.

The oxidizer mixture fed to the fuel cell consists of



## Solution of Problem 9.34

This is a total of 0.04165 kmols. Multiplying all by 72 will result in a total of 3 kmols, or considering the proportionality between kilomoles and pressure, we get the following partial pressures

Oxygen: 0.5 atmospheres,

Nitrogen: 2.0 atmospheres,

Water: 0.5 atmospheres.

As far as active gases are concerned, the fuel cell is fed hydrogen at 2.5 atmospheres and oxygen at 0.5 atmospheres. Thus the change in free energy owing to the reaction is

$$\begin{aligned}\Delta G &= -\Delta G_0 - RT(\ln 2.5 + 0.5 \ln 0.5) \\ &= -237.2 \times 10^6 - 8314 \times 298(\ln 2.5 + 0.5 \ln 0.5) \\ &= -238.6 \times 10^6 \text{ J/kmole.}\end{aligned}\quad (2)$$

The reversible voltage of the cell is

$$V_{rev} = \frac{-\Delta G}{2qN_0} = \frac{238.6 \times 10^6}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 1.239 \text{ V.} \quad (3)$$

The reversible voltage of the cell is 1.239 V.

**b - The fuel cell is connected to a 10 mΩ load. How much heat is generated internally by the cell?**

.....  
Except at very low load currents, the characteristics of the cell are given by

$$V_L = V_{oc} - R_{int}I_L - V_2 \ln \frac{I_L}{I_0}. \quad (4)$$

Most of the values in the equation above were given in the statement of the problem.

$$V_{oc} = V_{rev} - 0.139 = 1.239 - 0.139 = 1.10 \text{ V.} \quad (5)$$

$$V_2 = \frac{kT}{q\alpha} = \frac{1.38 \times 10^{-23} \times 298}{1.6 \times 10^{-19} \times 0.7} = 0.0367 \text{ V.} \quad (6)$$

$$V_L = 1.10 - 0.0051 I_L - 0.0367 \ln \frac{I_L}{0.60} \quad (7)$$

If  $R_L$  is the load resistance then,  $V_L = R_L I_L$ ,

$$1.10 - 0.0051 I_L - 0.0367 \ln \frac{I_L}{0.60} = 0.010 I_L. \quad (8)$$

**Solution of Problem 9.34**

$$0.0151 I_L + 0.0367 \ln \frac{I_L}{0.6} = 1.1 \quad (9)$$

The numerical solution of the above is  $I_L = 61.6$  A.

With such a current, the hydrogen consumption is

$$\dot{N} = \frac{I_L}{2qN_0} = \frac{61.6}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 3.20 \times 10^{-7} \text{ kilomoles/s.} \quad (10)$$

and the input power is

$$P_{in} = \Delta h \dot{N} = 285.9 \times 10^6 \times 3.20 \times 10^{-7} = 91.5 \text{ W.} \quad (11)$$

At a load current of 61.6 amperes, the power delivered to the load is

$$P_L = I_L^2 R_L = 61.6^2 \times 0.01 = 38.0 \text{ W.} \quad (12)$$

Consequently, a total of  $91.5 - 38.0 = 53.5$  watts of heat is shed by the fuel cell.

The fuel cell must shed 53.5 watts of heat.

**c - The fuel cell input gases contain water vapor (steam), and the fuel cell produces liquid water. Assume all of the water vapor contained in the input gases is lost. Does the fuel cell produce enough water to moistened the input gas streams when delivering the current of part b?**

.....  
The amount of product water produced when the load current is 61.6 A is  $3.20 \times 10^{-7}$  kilomoles per second.

For each kilomole of hydrogen used up, 0.2 kilomoles of water are required. Thus, at 61.6 A load current, the fuel side of the fuel cell needs  $0.2 \times 3.20 \times 10^{-7} = 0.64 \times 10^{-7}$  kilomoles of water every second.

On the oxidizer side, the oxygen consumption is  $1.60 \times 10^{-7}$  kilomoles per second and an identical amount of water is required. Thus, the water consumption is  $1.60 \times 10^{-7}$  kilomoles per second.

Total water consumption is  $0.64 \times 10^{-7} + 1.60 \times 10^{-7} = 2.24 \times 10^{-7}$  kilomoles per second which somewhat less the the rate of product water generation. Thus, in principle, the product water can be used to moisten the input gases.

There is enough product water to moisten the input gases.

## Solution of Problem 9.34



**Prob 9.35** The V-I characteristics of a fuel cell can be represented with reasonable accuracy, by the equation,

$$V_L = V_{oc} - R_{int}I_L - V_2 \ln \frac{I_L}{I_0}. \quad (1)$$

Let  $V_{oc} = 1.05$  V and  $R_{int} = 0.005$  ohms. When a 0.16-ohm load resistor is used, the current is 5.416 A, and when the load resistance is increased to 0.17 ohms, the current falls to 5.125 A.

What is the value of the constant,  $I_0$  in the formula?

*Do not use numerical or trial and error solutions.*

---

$R_L$	$I_L$	$V_L$
( $\Omega$ )	(A)	(V)
0.16	5.416	0.8666
0.17	5.125	0.8713

We completed the data given in the problem statement by using,

$$V_L = R_L I_L, \quad (2)$$

$$\frac{dV_L}{dI_L} = -R_{int} - \frac{V_2}{I_L}, \quad (3)$$

$$\frac{0.8666 - 0.8713}{5.416 - 5.125} = -0.01615 = -0.005 - \frac{V_2}{I_{mean}}, \quad (4)$$

$$I_{mean} = \frac{5.416 + 5.125}{2} = 5.271, \quad (5)$$

$$V_2 = (0.01615 - 0.005) \times 5.271 = 0.05877 \quad (6)$$

To find  $I_0$ , we use Equation 1,

$$0.8666 = 1.05 - 0.005 \times 5.416 - 0.05877 \ln \frac{5.416}{I_0}. \quad (7)$$

$$\ln \frac{5.416}{I_0} = 2.660, \quad (8)$$

$$I_0 = \frac{5.416}{\exp 2.666} = 0.38. \quad (9)$$

$I_0 = 0.38$

## Solution of Problem 9.35

**Prob 9.36** A lab test of a hydrogen/oxygen fuel cell consisted of adjusting the load resistance,  $R_L$ , until a preselected load current,  $I_L$ , was precisely achieved. This yielded the results tabulated below:

$R_L$ ( $\Omega$ )	$I_L$ (A)
1.0643	1.000
0.1944	5.000
0.0129	50.00

a – What power does the fuel cell deliver to the load when  $I_L = 20$  A?

b – What is the activation voltage when  $I_L = 20$  A?

c – By using the data for 1 A and 50 A, estimate a value for  $R_{app}$ , and using this value estimate the power delivered to the load when  $I_L = 20$  A.

The open-circuit voltage of the cell (at 90 C which is the operating temperature in this problem) is 1.10 V.

.....  
The characteristics of the fuel cell can be represented with good accuracy by,

$$V_L = V_{oc} - R_{int}I_L - V_2 \ln \left( \frac{I_L}{I_0} \right) \quad (1)$$

We have here three unknown parameters,  $R_{int}$ ,  $V_2$ , and  $I_0$ . We need three independent equations that must be solved simultaneously. With a certain amount of work, one finds,

$$R_{int} = 0.00491 \quad \Omega,$$

$$V_2 = 0.0449 \quad \text{V},$$

$$I_0 = 0.5 \quad \text{A}.$$

Consequently,

$$V_L = 1.10 - 0.00491I_L - 0.0449 \ln \left( \frac{I_L}{0.5} \right). \quad (2)$$

With a 20 A load current,  $V_L = 0.836\text{V}$ , and the power delivered to the load ( $P_L = I_L V_L$ ) is 16.7 W.

The power delivered to the load is 16.7 W.
--

The activation voltage is,

$$V_{act} = V_2 \ln \left( \frac{I_L}{I_0} \right) = 0.0449 \ln \left( \frac{20}{0.5} \right) = 0.165 \quad \text{V..} \quad (3)$$

## Solution of Problem 9.36

The activation voltage is 165 mV.

$$R_{app} = \frac{1.064 - 0.644}{50 - 1} = 0.0086 \quad \Omega. \quad (4)$$

$$V_L = 1.10 - 0.0086 \times 20 = 0.928 \quad \text{V}. \quad (5)$$

$$P_L = 20 \times 0.928 = 18.6 \quad \text{W}. \quad (6)$$

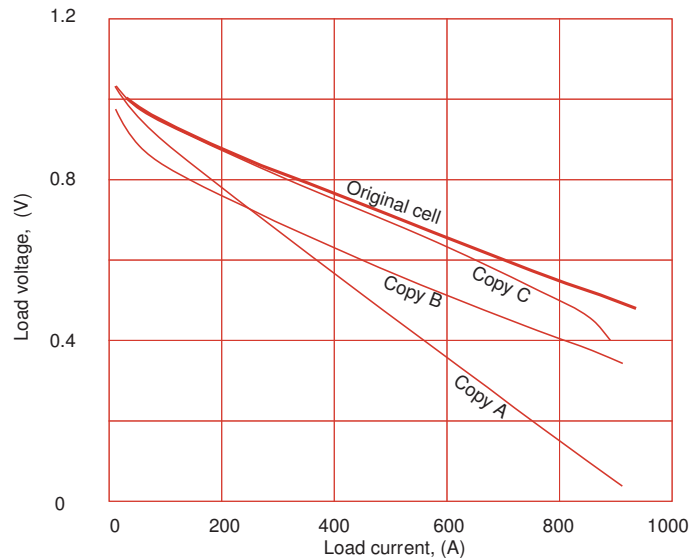
The power delivered to the load is 18.6 W.

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Solution of Problem 9.36

**Prob 9.37** All answers must be short and terse. No dissertations, please.

A fuel cell manufacturer has accurate data on a rival manufacturer's solid polymer, hydrogen/oxygen fuel cell known for its excellent performance. The data are plotted in the figure and are labeled "Original Cell".



The development department of the first manufacturer did its best to build a cell identical to the original, but had limited success as demonstrated by the  $V$ - $I$  plot labeled "Copy A". All copies operate at the same temperature and pressures as the original. They all were fed pure, uncontaminated, hydrogen and clean air.

a – Identify the one error made in this cell. What tipped you off? What would you do to rectify this error?

Observation:

Copy A of the fuel cell has a much greater slope in its  $V$ - $I$  plot than the original.

Probable reason:

A much larger  $R_{int}$  than that of the original.

Correction:

- Reduce electrode thickness
- Make sure electrolyte is neither desiccated nor dry. Improve water management.

## Solution of Problem 9.37

- Consider using a better membrane, perhaps one with smaller equivalent weight.
- Check operating temperature. Perhaps it is too low.

**b – Do the same for “Copy B.**

Observation:

Copy B has a  $V$ - $I$  slope very near that of the original. This suggests that the internal resistance is about the same in both cells. However, the characteristics have a lot of curvature and this leads to substantially lower load voltage.

Probable reason:

Activation losses are too high. There is something wrong with the catalysis.

Correction:

- Check the catalytic loading of the MEA.
- Again, check operating temperature. Perhaps it is too low.

**c – Do the same for “Copy C.**

Observation:

Copy C performs nearly as well as the original, at low currents, but departs from it at high currents.

Probable reason:

This cell seems to have too many transport losses.

Correction:

- Examine the gas flow plates.
- Examine electrode porosity.
- Check for drowning of the electrodes.

**d – In addition to the three copies of the original fuel cell whose characteristics appear in the figure, there is a fourth copy (Copy D) that has a plot almost exactly parallel to that of the original but is, roughly, 0.1 lower in voltage. For this one, also, answer the questions as before.**

Observation:

Copy D has a  $V$ - $I$  shape similar to the original but shifted down in voltage.

Probable reason:

Unwanted side reactions, fuel cross-over generating a counter voltage.

Correction:

- Check for excessive permeability of the electrolyte
- Check for pin holes or for inadequate electrolyte thickness.

## Solution of Problem 9.37

**Prob 9.38** Let us compare the performances of two different fuel cell cars, one equipped with a small fuel cell (SFC) and one with a large fuel cell (LFC). The SFC car has slightly more power than the average power needed for the trip, while LFC car has much more power than the average needed and is capable of fast accelerations and can climb steep hills at a pretty good clip—it is much more “sexy”. In this particular test, the cars drive on a flat, horizontal road with no external wind. They drive at the same uniform speed and the fuel cell (in both cases) delivers a steady 10 kW to the wheels. Either fuel cell is actually a battery of 250 elementary, hydrogen/air, fuel cells connected in series. In order to simplify calculations, model the elementary fuel cell as a voltage generator (open-circuit voltage,  $V_{oc} = 1.0$  V), in series with an internal resistance,  $R_{int}$ .

In the case of SFC,  $R_{int} = 0.0055$  ohms, in in the case of LFC,  $R_{int} = 0.0011$  ohms. In either case water vapor is produced by the reaction.

Assume that the trip lasts exactly 5 hours and that the cars travel at a constant speed of 90 km/h. Calculate (for both SFC and LFC):

a – How many kg of hydrogen will be consumed.

.....  
Observe that the two fuel cells may be rather similar in construction. The only difference may be that the larger one (LFC) has an active electrode area 5 times that of the smaller. If so, the stack length of the two will be roughly the same, only the crosssectional area differs. In such a case the mass of the two cells will be proportional to the power. One can gain some feeling of the number involved by looking at the Ballard Mark 1100 cell that delivers 110 kW (continuous power) and masses 120 kg—a gravimetric power density of 0.76 kW/kg. The continuous power the cells in this problem will have to deliver is 10 kW. Assuming that this is all the small cell would have to deliver, it would mass some 13 kg. The larger one, which would normally operate at only a small fraction of its rated power, would mass some 65 kg. Compare with the mass of a Prius: 1,300 kg.

The average power per elementary cell is  $P_{ave} = \frac{10,000}{250} = 40$  W per cell.

The load voltage is

$$V_L = 1.0 - R_{int}I_L. \quad (1)$$

The load power is

$$P_L = I_L - R_{int}I_L^2 = 40 \text{ W}, \quad (2)$$

## Solution of Problem 9.38

This quadratic equation has two roots, only the smaller one makes sense from the engineering point of view. The larger one would correspond to much bigger fuel consumption.

$$I_L = \begin{cases} 59.4 & A \quad (SFC) \\ 41.9 & A \quad (LFC) \end{cases} \quad (3)$$

This corresponds to a hydrogen consumption of

$$\dot{N} = \frac{I_L}{2qN_0} = \frac{I_L}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 5.18 \times 10^{-9} I_L \quad \text{kmole H}_2/\text{s}. \quad (4)$$

The above is per cell. Per battery for 5 hours,

$$C = 250 \times 5 \times 3600 \times 2 \times 5.18 \times 10^{-9} I_L = 0.0466 I_L \quad \text{kg H}_2 \quad (5)$$

$$C = \begin{cases} 2.76 & \text{kg(H}_2) \quad (SFC) \\ 1.95 & \text{kg(H}_2) \quad (LFC) \end{cases} \quad (6)$$

**b – How much reserve power,  $P_{acc}$ , is available for surges, i.e., what is the difference between the maximum power the battery can deliver and the steady power needed for driving the car at the specified speed.**

The maximum power each cell can deliver is

$$P_{L_{max}} = \frac{V_{oc}^2}{4R_{int}} = \frac{0.25}{R_{int}} \quad \text{W}. \quad (7)$$

because, for maximum power transfer,  $R_{load} = R_{int}$ . The maximum power the battery can deliver is

$$P_{L_{batt_{max}}} = \frac{62.5}{R_{int}} \quad \text{W}. \quad (8)$$

$$P_{L_{batt_{max}}} = \begin{cases} 11,360 & \text{W.} \\ 56,800 & \text{W.} \end{cases} \quad (9)$$

The margin for acceleration of the car is

$$P_{acc} = \begin{cases} 11,360 - 10,000 = 1,360 & \text{W.} \quad \text{SFC} \\ 56,800 - 10,000 = 46,800 & \text{W.} \quad \text{LFC} \end{cases} \quad (10)$$

---

## Solution of Problem 9.38

**c – Select either the SFC or the LFC car as the one you would recommend for production. Defend your selection by pointing out the advantages and disadvantages of the two types.**

.....  
Somewhat counterintuitively, the larger fuel cell yields a better “kilometrage” [km/kg(H<sub>2</sub>)] than the smaller one and has a great edge in its surge capacity. From the performance point of view, there can be no doubt that the LFC is much better. The question that remains is one of cost. Clearly, the SFC is cheaper. But is it significantly cheaper? It has 1/5 of the power of the LFC and that gives it, very roughly, a 5:1 cost advantage in the fuel cell, which is only a fraction of the overall cost. Assume that the large fuel cell cost is 25% of the car cost, then, the cheaper car will cost 80% of the cost of the larger. That is for instance, the difference between \$30,000 and \$24,000.

This price advantage will be eroded by the larger cost of the hydrogen storage system of the SFC (assuming equal range for both cars). The SFC car uses 40% more fuel than the LFC. This will increase correspondingly the mass of the storage system of the smaller car compensating, partially, the larger mass of the fuel cell in the larger car.

The customer will have to make a choice between a more expensive car that is sexier and more fuel-economic, and a smaller cheaper but very sluggish hydrogen hogger. I, personally, would opt for the bigger car.

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## Solution of Problem 9.38



**Prob 9.39** A given electric car experiences a retarding force given by

$$F = 80 + 5v + 0.25v^2, \quad (1)$$

where  $v$  is the velocity of the car.

Assume a straight, horizontal, windless highway.

The car carries 20 lead-acid batteries connected in series, each having a 300 Ah capacity when discharged at a steady 15 A current. The batteries have a Peukert number of 1.2. Assume that the open-circuit voltage of each battery is 12.0 V independently of the state of charge, SOC. Each battery has an internal resistance of 40 milliohms.

a - What is the range of the car when the electric motor (100% efficient) is running at a current of 15 A? .....  
 ..... The load voltage of each battery, under a 15 A current is

$$V_L = V_{oc} - R_{int}I_L = 12 - 0.04 \times 15 = 11.4 \text{ V}. \quad (2)$$

Each battery delivers  $11.4 \times 15 = 171$  W. All batteries together deliver  $171 \times 20 = 3,420$  W.

The power that propels the car is

$$P = Fv = 80v + 5v^2 + 0.25v^3. \quad (3)$$

This cubic equation is best solved numerically. For  $P = 3420$  W, it yields  $v = 15.6$  m/s or 56.2 km/h. A bit slow, but the car can sustain this speed for 20 hours and consequently covers a distance of  $20 \times 56.2 = 1,124$  km, an excellent range!

The range of the car is 1,124 km.

b - Assume that you want to cruise at 85 km/hr. What is the car's range? .....  
 ..... To maintain a speed of 85 km/h (23.6 m/s) the power required (Equation 3) is 7,967 W. Each battery has to deliver  $7,959/20 = 398$  W.

$$P_L = V_{oc}I_L - R_{int}I_L^2, \quad (4)$$

$$398 = 12I_L - 0.04I_L^2. \quad (5)$$

The solution is  $I_L = 38$  A.

We have, now, to calculate what the capacity of the battery is when delivering a steady 38 A. Remember that the original capacity of the battery was  $C_0 = 300$  Ah when the discharge rate was a steady 15 A.

## Solution of Problem 9.39

The capacity of the battery is

$$C = \Lambda \times I^{1-n} \quad (6)$$

where, in this problem,  $n$  is given as 1.2, and  $\Lambda$  must be calculated from

$$\Lambda = C_0 I^{n-1} = 300 \times 15^{1.2-1} = 516 \quad (7)$$

$$516 \times 38^{1-1.2} = 249 \text{ Ah.} \quad (8)$$

249 Ah at 38 A corresponds to 6.55 hours which, at 80 km/h, will drive the car 557 km.

At 80 km/h, the car will have a range of only 557 km.

## Solution of Problem 9.39

**Prob 9.40**    Examine the chemical equation,



Both A and B have each a standard enthalpy of formation,  $\Delta \bar{h}f^\circ$ , of 0 and an entropy,  $\bar{s}^\circ$ , of  $60 \text{ kJ K}^{-1}\text{kmole}^{-1}$ . All quantities in this problem are independent of temperature.

For each of the cases below:

Will the reaction proceed at room temperature? Will it proceed at 1000 K?

**a – The product, AB, has a  $\Delta \bar{h}f^\circ = -100 \text{ MJ/kmole}$ , and a  $\bar{s}^\circ = 10 \text{ kJ K}^{-1}\text{kmole}^{-1}$ .**

.....  
The  $\Delta H$  owing to the reaction is  $-100 \text{ MJ/kmole}$ . This decrease in enthalpy (exothermic reaction) favors the reaction.

On the other hand, the entropy of the reactants,  $120 \text{ kJ K}^{-1}\text{kmole}^{-1}$ , disappears and is replaced by the  $10 \text{ kJ K}^{-1}\text{kmole}^{-1}$  entropy of the product. This decrease,  $\Delta S = -110 \text{ kJ K}^{-1}\text{kmole}^{-1}$ , in entropy opposes the reaction.

The free energy change is  $\Delta G = \Delta H - T\Delta S$  will decide which effect dominates

At 298 K,  $\Delta G = -100 - 298 \times (-0.11) = -67.2 \text{ MJ/kmole}$ .  
This negative value indicates that the reaction will proceed.

At 1000 K,  $\Delta G = -100 - 1000 \times (-0.11) = 10 \text{ MJ/kmole}$ .  
This positive value indicates that the reaction will not proceed.

---

**b – The product, AB, has a  $\Delta \bar{h}f^\circ = -100 \text{ MJ/kmole}$ , and a  $\bar{s}^\circ = 150 \text{ kJ K}^{-1}\text{kmole}^{-1}$ .**

.....  
In this case, the reaction is still exothermic and is favored by this circumstance. The product has more entropy than the reactants and this also favors the reaction.

The reaction proceeds at both 298 K and 1000 K.

---

**The product, AB, has a  $\Delta \bar{h}f^\circ = 10 \text{ MJ/kmole}$ , and a  $\bar{s}^\circ = 150 \text{ kJ K}^{-1}\text{kmole}^{-1}$ .** .....

.....  
This is an endothermic reaction ( $\Delta Hf^\circ = 10 \text{ MJ/kmole}$ ), its energy balance hinders the reaction. However, the entropy change is positive ( $\Delta S = 30 \text{ kJ K}^{-1}\text{kmole}^{-1}$ ) which helps the reaction.

The free energy change is  $10 - 0.03T$ .

## Solution of Problem    9.40

At 298 K, the change of free energy is 1.06 MJ/kmole, a positive value that shows that the reaction will not proceed. However, at 1000 K, the change in free energy is -20 MJ/kmole and the reaction will proceed.

Q.	$\Sigma\Delta H_f^\circ$	$\Sigma\Delta H_f^\circ$	$\Delta H$	S	S	$\Delta S$	$\Delta G$	$\Delta G$	React.	
	React.	Prod.	Reaction	React.	Prod.	Reaction	298 K	1000 K	298 K	1000 K
a	0	-100	-100	0.12	0.01	-0.11	-67.2	10	<b>Y</b>	<b>N</b>
b	0	-100	-100	0.12	0.15	0.03	-108.4	-130	<b>Y</b>	<b>Y</b>
c	0	10	10	0.12	0.15	0.03	1.06	-20	<b>N</b>	<b>Y</b>

## Solution of Problem 9.40

**Prob 9.41** By towing a car on a horizontal road on a windless day, at sea level, and inserting a dynamometer in the tow line, it was possible to determine the force needed to keep the car rolling at a variety of different velocities. The data obtained fit quite well the formula below

$$F = 120 + 10v + 0.3v^2 \quad \text{N.} \quad (1)$$

The car, massing 1200 kg, is driven by a fuel cell battery consisting of 300 series connected cells each of which has the  $V$ - $J$  characteristics given by

$$V_L = 0.95 - 1 \times 10^{-5} J_L. \quad (2)$$

a – You can choose the active area of each cell. Although this is not possible, imagine that you did choose cells with infinite active area. Calculate how much hydrogen would be used to drive the car 300 km on a flat, horizontal windless road at sea level at a speed of 100 km/hr. Assume that the electric driving system is 100% efficient.

.....  
100 km/h correspond to 27.78 m/s. At this speed the power used is

$$\begin{aligned} P_{total} &= vF = 120v + 10v^2 + 0.3v^3 \\ &= 120 \times 27.78 + 10 \times 27.78^2 + 0.3 \times 27.78^3 = 17,479 \quad \text{W.} \end{aligned} \quad (3)$$

Per cell, the power is

$$P_L = \frac{17,479}{300} = 58.26 \quad \text{W.} \quad (4)$$

Note that  $R_{int} = \frac{\mathfrak{R}}{A} = 0$ , where  $A$  is the area of the cell (infinite, in this case). The  $V$ - $I$  characteristics reduces to

$$V_L = 0.95 \quad (5)$$

and the power delivered to the load is

$$P_L = 0.95I_L = 58.26 \quad \text{W,} \quad (6)$$

hence,  $I_L = \frac{58.26}{0.95} = 61.33 \quad \text{A.}$

$$\begin{aligned} \dot{N} &= \frac{I_L}{2qN_0} = \frac{61.33}{2 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{26}} \\ &= 3.18 \times 10^{-7} \quad \text{kmoles(hydrogen)/sec.} \end{aligned} \quad (7)$$

The trip last 3 hours or 10,800 seconds, therefore the hydrogen consumption is  $300 \times 10,800 \times 3.18 \times 10^{-7} = 1.03$  kmoles or 2.06 kg of hydrogen.

The trip would use up 2.06 kg of hydrogen.

## Solution of Problem 9.41

**a' – Another solution**

.....  
 The force,  $F$ , necessary to keep the carat a steady 27.78 m/s is 630 newtons. The trip is 300,000 m long hence the energy expended is  $630 \times 300,000 = 189$  MJ. An ideal fuel cell produces, at RTP, 228 MJ of electricity per kilomole of hydrogen used up. Consequently, the number of kmole use in the trip is  $189/228 = 0.823$  kmoles of hydrogen.

But the cell is not ideal. Instead of 1.185 V, it generates only 0.95 V. Thus, we have to multiply the amount of hydrogen use by  $1.185/0.95 = 1.247$ . This yields a hydrogen consumption of  $0.823 \times 1.247 = 1.03$  kmoles of  $H_2$ . This is, exactly, what we got in the previous solution.

**b – What is the smallest cell area that still would allow the trip to be completed in 3 hr? What is the power density (in W/cm<sup>2</sup>) of the cell? How much hydrogen would be used up?**

.....  
 The maximum power that this particular cell can deliver occurs when the load resistance equals the internal resistance of the cell. When this occurs, the load voltage must be half of the open-circuit voltage and the power delivered to the load is

$$P_L = \frac{(\frac{1}{2}V_{oc})^2}{R_{int}} = \frac{(\frac{1}{2} \times 0.95)^2}{R_{int}} = 58.26 \text{ W}. \quad (8)$$

This leads to  $R_{int} = 0.00387 \text{ } \Omega$ . Since  $A = \frac{\mathcal{R}}{R_{int}}$ , we get an area of

$$A = \frac{10^{-5}}{0.00387} = 0.00258 \text{ m}^2 \text{ or } 25.8 \text{ cm}^2. \quad (9)$$

The cell operates at a power density of

$$P_{dens} = \frac{58.26}{25.8} = 2.26 \text{ W/cm}^2. \quad (10)$$

(This is a bit high, the cell may overheat.)

The current through the cell is

$$I_L = \frac{\frac{1}{2}V_{oc}}{R_{int}} = \frac{\frac{1}{2} \times 0.95}{0.00387} = 122.7 \text{ A}. \quad (11)$$

The fuel consumption is

$$\begin{aligned} \dot{N} &= \frac{I_L}{2qN_0} = \frac{122.7}{2 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{26}} \\ &= 6.37 \times 10^{-7} \text{ kmoles(hydrogen)/sec.} \end{aligned} \quad (11)$$

## Solution of Problem 9.41

This is per cell and per second. The trip lasts 10,800 seconds and require 300 cells, hence the consumption is 2.06 kmols or 4.13 kg of hydrogen.

The smallest cell area that will permit a trip time of 3 hours is 25.8 cm<sup>2</sup>.  
The cell will deliver 2.26 W/cm<sup>2</sup> and use up 4.13 kg of hydrogen.

**c – Assume that the only cells available have an active area 98.7% of the minimum required as calculated in Part b of this problem. This means that you cannot quite satisfy the requirements established in Part a (300 km at 100 km/h, flat, level road, no wind, sea level). However, the hydrogen you are using comes from a very high pressure canister and was throttled down to the 1 atmosphere specified in Part a. By what factor do you have to increase the hydrogen pressure delivered to the cells to make the trip possible assuming that all other conditions are kept the same as before? Please comment.**

.....  
98.7% of 25.8 cm<sup>2</sup> is 25.46 cm<sup>2</sup>. Cells with 25.46 cm<sup>2</sup> of active area have an internal resistance of

$$R_{int} = \frac{Re}{A} = \frac{10^{-5}}{25.46 \times 10^{-4}} = 0.003928 \quad \Omega, \quad (12)$$

For such cells to deliver 58.26 W, they must have an open-circuit voltage,  $V_{oc}$ , that satisfies:

$$P_L = \frac{(\frac{1}{2}V_{oc})^2}{R_{int}} = \frac{(\frac{1}{2}V_{oc})^2}{0.003928} = 58.26 \quad (13)$$

from which,  $V_{oc} = 0.9567$  V. This means that the open-circuit voltage has to grow by (0.9567-0.95=0.0067) V.

The free energy rise of the hydrogen gas (per kilomole) over the original RTP conditions is (when converted to voltage)

$$V = \frac{RT \ln(p/p_0)}{2qN_0} = \frac{8314 \times 298 \ln((p/p_0))}{2 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{26}} = 0.0067. \quad (14)$$

Consequently,

$$\ln(p/p_0) = 0.5521, \quad (15)$$

or

$$p/p_0 = 1.68. \quad (16)$$

The hydrogen would have to be pre-compressed by a factor of 1.68.

## Solution of Problem 9.41

**Prob 9.42** A fuel cell has the  $V$ - $J$  characteristics given by

$$V = 1.00 - 10^{-5} J \quad (1)$$

where  $J$  is the current density in  $\text{A m}^{-2}$ .

The mass of the cell is 15 kg for each  $\text{m}^2$  of active surface.  $N$  cells must be connected in series to produce 12 volts while supplying 12 kW. The battery must be able to do this for one week. Since the cells will operate in a satellite, it is important to minimize the total mass. To do this, how many cells do you have to use? What is the total mass?

.....  
Minimum mass occurs when a cell delivers maximum power:

$$P = VJ = J - 10^{-5} J^2, \quad (2)$$

$$\frac{dP}{dJ} = 1 - 2 \times 10^{-5} J, \quad (3)$$

$$J = 50,000 \text{ A/m}^2, \quad (4)$$

$$V = 1 - 10^{-5} \times 50,000 = 0.5 \text{ V}. \quad (5)$$

Since we need 12 V, the number of cells is  $N = 24$ , and since the cell has to deliver 12,000 W,

$$I = \frac{12,000}{12} = 1,000 \text{ A}, \quad (6)$$

$$A = \frac{I}{J} = \frac{1,000}{50,000} = 0.02 \text{ m}^2, \quad (7)$$

$$M = 15NA = 15 \times 24 \times 0.02 = 7.2 \text{ kg}. \quad (8)$$

The mass of the battery is 7.2 kg.
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## Solution of Problem 9.42



**Prob 9.43** Very accurate measurements of the  $V$ - $I$  characteristics of a fuel cell allowed the determination of its slope. It was found that at 10 A, the slope was -0.003 V/A but at 5A the slope was much larger (in absolute value), -0.005 V/A. Does this make sense? If so, can you tell me what the internal resistance of the cell is?

.....  
The  $I$  vs  $V$  characteristic of a fuel cell can be represented mathematically by

$$V_L = V_{OC} - R_{int}I - V_{act}, \quad (1)$$

A good approximation for the dependence of  $V_{act}$  on  $I$  (unless  $I$  is very small) is

$$V_{act} = V_2 \ln \frac{I}{I_0}. \quad (2)$$

In this case,

$$V_L = V_{OC} - R_{int}I - V_2 \ln \frac{I}{I_0}. \quad (3)$$

$$\frac{V_L}{dI} = -R_{int} - \frac{V_2}{I}. \quad (4)$$

We can now set-up a pair of simultaneous equations,

$$\begin{cases} -0.005 = -R_{int} - \frac{V_2}{5}, \\ -0.003 = -R_{int} - \frac{V_2}{10}. \end{cases} \quad (5)$$

which yield

$$R_{int} = 0.001 \quad \Omega$$

and

$$V_2 = 0.02 \quad \text{V}.$$

The true internal resistance of the cell is 1 milliohms

## Solution of Problem 9.43

