

Chapter 10

Hydrogen Production

Problem Solutions



**Prob 10.1** Let  $C_D$  be the price of an electrolyzer installation expressed in dollars per kW of hydrogen produced when a given current density,  $J_0$  is employed. The number of output kW is that heat power that would be generated if the produced hydrogen were burned. There is no compelling reason to operate the electrolyzer at the nominal ( $J_0$ ) current density. It can be operated at any other current density,  $J$ , within the permissible range.

The cost of the hydrogen produced,  $C_H$ , is

$$C_H = C_{INV} + C_{OP} + C_E \quad \text{\$/(\text{kg of H}_2\text{)}}$$

where

$C_{INV}$  = part of the cost attributable to the cost of investment in the plant,

$C_{OP}$  = the maintenance and operation cost (assume this to be zero), and

$C_E$  = the cost of the electric energy which is a function of  $c_e$ , the price of electricity.

Assume that the efficiency of the electrolyzer depends linearly on the current density:

$$\eta = a + bJ.$$

Let  $\Theta$  be the plant factor—that is, the fraction of the total time during which the plant is actually operating.

Let  $R$  be the yearly cost of the capital—that is, the interest, taxes, insurance, etc., expressed as a fraction of the borrowed capital.

Develop an expression that yields the value of  $J$  that minimizes the cost of the hydrogen produced. This must be a function of  $C_D$ ,  $J_0$ ,  $R$ ,  $\Theta$ ,  $c_e$ ,  $a$ , and  $b$ .

What is this optimum value of  $J$  for the case in which

$$\begin{aligned} C_D &= 100 \text{ \$/kW}, \\ J_0 &= 10,000 \text{ A/m}^2, \\ R &= 0.2 \text{ per year}, \\ \Theta &= 1, \\ c_e &= 10 \text{ \$/MWh}, \\ a &= 0.74, \\ b &= -6 \times 10^{-6} \text{ m}^2/\text{A}. \end{aligned}$$

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The manufacturer of the electrolyzer will sell you the equipment for an agreed price,  $\Pi$ , and will quote a specified hydrogen production rate,  $P_{H_2}$  in kilowatts of hydrogen<sup>†</sup>. Of course, this rate assumes that the equipment

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<sup>†</sup> The production rate is quoted in terms of the rate of heat produced if the hydrogen is burned at RTP.

## Solution of Problem 10.1

is operated at a suggested current density,  $J_0$ . This means that the price can be specified in terms of dollars per kilowatt:

$$C_D \equiv \frac{\Pi}{P_{H_2}}.$$

If the buyer decides to operate the electrolyzer at a different current density,  $J$ , the price per kW will be different (it is a function of  $J$ .) even though the amount of money paid for the equipment is still the same,

Since the production rate is proportional to the current density, the price per kW of hydrogen produced is now

$$C_D \frac{J_0}{J} \quad \$/\text{kW (H}_2\text{)}.$$

This is exactly the same as buying a 220 V, 2 kW electric motor for, say \$200 (\$100/kW) and the operating it at, say 250 V. The motor will develop a larger power output and, consequently the cost per kW is now less than 100\$/kW. The motor may also overheat and blow up, but that is a separate consideration.

The yearly cost of investment,  $C_{inv, year}$ , can also be expressed in terms of kW of hydrogen. It is, simply,

$$C_{inv, year} = C_D \frac{J_0}{J} R \quad \$/\text{kW per year}.$$

This assumes that the plant operates continuously, all the time ( $\Theta = 1$ ). For a plant that operates intermittently,

$$C_{inv, year} = C_D \frac{J_0}{J} \frac{R}{\Theta} \quad \frac{\$}{\text{kJ year}}.$$

We replaced kW by kJ/s. Since there are  $31.6 \times 10^6$  seconds in a year,

$$C_{inv} = C_D \frac{J_0}{J} \frac{R}{\Theta} \frac{1}{31.6 \times 10^6} \quad \$ \text{ per kJ of hydrogen}.$$

The producer may want to quote the price of hydrogen in dollars per kg. Since 1 kg of  $H_2$  has a higher heat value of 143,000 kJ,

$$C_{inv} = C_D \frac{J_0}{J} \frac{R}{\Theta} \frac{143 \times 10^3}{31.6 \times 10^6} = 4.52 \times 10^{-3} C_D \frac{J_0}{J} \frac{R}{\Theta} \quad \$ \text{ per kg of hydrogen}.$$

The cost,  $C_H$ , of the produced hydrogen is the sum of the investment cost and the plant operation cost. The latter includes personnel, electric energy, etc. Let us consider only the cost of electric energy,  $C_E$ , which is

$$C_E = 143 \frac{\text{MJ}}{\text{kg}} \times \frac{1}{\eta} \times c_e \frac{\$}{\text{MJ}} \quad \$ \text{ per kg of hydrogen}.$$

In the above,  $c_e$  is in dollars per MJ. The problem states that the cost of electricity is \$10/MWh which converts to 0.002778 \$/MJ. Observe the number of significant figures when one talks about costs!

$$C_H = C_{inv} + C_E = 4.52 \times 10^{-3} C_D J_0 \frac{R}{\Theta} \times \frac{1}{J} + 143 \frac{c_e}{\eta(J)}.$$

## Solution of Problem 10.1

Defining,

$$A \equiv 4.52 \times 10^{-3} C_D J_0 \frac{R}{\Theta}$$

and

$$B \equiv 143 c_e,$$

we can write

$$C_H = \frac{A}{J} + \frac{B}{\eta} \quad \$ \text{ per kg of hydrogen.}$$

As indicated,  $\eta$  is a function of  $J$ .

An extremum in the cost of hydrogen can be found:

$$\frac{dC_H}{dJ} = -\frac{A}{J^2} - \frac{B}{\eta^2} \frac{d\eta}{dJ}.$$

But

$$\eta = a + bJ,$$

$$\frac{dC_H}{dJ} = -\frac{A}{J^2} - \frac{Bb}{(a+bJ)^2} = 0.$$

$$\frac{A}{J^2} = -\frac{Bb}{(a+bJ)^2},$$

$$Aa^2 + Ab^2J^2 + 2AabJ + BbJ^2 = 0$$

$$(Ab^2 + Bb)J^2 + 2AabJ + Aa^2 = 0,$$

$$J = \frac{-2Aab \pm \sqrt{4A^2a^2b^2 - 4A^2a^2b^2 - 4Aa^2Bb}}{2Ab^2 + 2Bb}$$

$$= \frac{-2Aab \pm \sqrt{-4Aa^2Bb}}{2(Ab^2 + Bb)} = \frac{-Aab \pm \sqrt{-Aa^2Bb}}{Ab^2 + Bb},$$

$$A = 4.52 \times 10^{-3} \frac{C_D J_0 R}{\Theta} = 904,$$

$$B = 143 \times 0.002778 = 0.397,$$

$$a = 0.74,$$

$$b = -6 \times 10^{-6},$$

$$J = \frac{904 \times 0.74 \times 6 \times 10^{-6} - \sqrt{904 \times 0.74^2 \times 0.397 \times 6 \times 10^{-6}}}{904 \times (6 \times 10^{-6})^2 - 0.397 \times 10^{-6}}$$

$$= \frac{0.00401 - 0.03434}{-2.349 \times 10^{-6}} = 12,900 \quad \text{A m}^{-2}.$$

The current density that leads to the lowest hydrogen cost is  
12,900 A m<sup>-2</sup>.  
Must check with manufacturer to  
determine if this current is allowed.

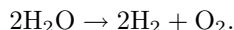
## Solution of Problem 10.1

**Prob 10.2** An electrolytic cell having 100% current efficiency, operates at a voltage of 1.9 V when the current is 20 kA. Its operating temperature is 86 C. The cell happens to be completely heat insulated: heat can only be removed by the flow of reactants and of products and by water flowing through a cooling system built into the cell.

Both feed and cooling water enter the system at 25 C. The cooling water leaves at 80 C. The gases leave at 85 C. Assume that the enthalpy change owing to the reaction is independent of temperature (-285.9 MJ per kilomole of water).

**a. What is the hydrogen production rate in kg/hour?**

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The overall reaction in the electrolyzer is



To produce 1 kilomole of  $\text{H}_2$  (or to consume 1 kilomole of  $\text{H}_2\text{O}$ ), 2 kilomoles of electrons are involved. This corresponds to a charge of  $2 \times 1.6 \times 10^{-19} 6 \times 10^{26} = 193 \times 10^6$  coulombs per kilomole of  $\text{H}_2$ .

The current is 20 kA or  $2 \times 10^4$  coulombs/second. Thus, the rate of production of hydrogen is

$$\frac{2 \times 10^4 \text{ coulombs}}{193 \times 10^6 \text{ second}} \times \frac{\text{kmoles H}_2}{\text{coulomb}} = 1.04 \times 10^{-4} \frac{\text{kmoles (H}_2)}{\text{second}},$$

or

$$1.04 \times 10^{-4} \frac{\text{kmoles (H}_2)}{\text{second}} \times 2 \frac{\text{kg (H}_2)}{\text{kmoles (H}_2)} = 2.08 \times 10^{-4} \frac{\text{kg (H}_2)}{\text{second}},$$

or

$$0.746 \frac{\text{kg (H}_2)}{\text{hour}}.$$

The electrolyzer produces 0.746 kg of hydrogen per hour.

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**b. What is the feed water consumption rate?**

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For each kilomole of  $\text{H}_2$ , one kilomole of  $\text{H}_2\text{O}$  is used up. But,  $\text{H}_2\text{O}$  has a molecular mass 9 times larger than  $\text{H}_2$ . Thus, the amount of water consumed is

$$9 \times 0.746 = 6.71 \text{ kg (H}_2\text{O) per hour.}$$

The electrolyzer consumes 6.71 kg of water per hour.

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## Solution of Problem 10.2

### c. What is the flow rate of the cooling water?

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The input power to the cell is

$$P_{in} = 1.9 \text{ V} \times 20,000 \text{ A} = 38,000 \text{ W}.$$

When the cell voltage is

$$\frac{\Delta H}{2qN_0} = \frac{285.9 \times 10^6}{2 \times 1.6 \times 10^{-19} \times 6 \times 10^{26}} = 1.484 \text{ V},$$

the electrolysis proceeds with no heat exchange, i.e., it is neither endothermic nor exothermic. Consequently, an amount of power,  $(1.9 - 1.484) \times 20,000 = 8320$  watts is transformed into heat and must be removed. We used 285.9 MJ/kmole and 1.484 V for, respectively, the higher heat of combustion and the “isothermal” operation voltage (values appropriate for RTP) because the statement of the problem recommends RTP values. More correctly, they should be adjusted to 86 C and should be 286.3 MJ/kilomole and 1.486 V. But this would lead to only slightly different results.

A small part of this heat is removed by the feed water that enters the electrolyzer at 25 C. It is not entirely clear how much this part amounts to. In one extreme, one can imagine that the water heats up to the operating temperature of the electrolyzer before being split apart. In this case the heat removed by the feed water is

$$P_{feed \text{ water}} = \frac{4180 \times 6.71 \times 60}{3600} = 470 \text{ W}.$$

In the above, 4180 is the heat capacity of water in J/K per kilogram and 60 is the temperature change in kelvins.

In the other extreme, one can imagine that the water is electrolyzed at 25 C and the resulting gases then heat up to the operating temperature of 85 C. The production rate of hydrogen is  $1.04 \times 10^{-4}$  kilomoles per second and that of oxygen is one half of this amount. The total gas production is  $1.56 \times 10^{-4}$  kilomoles per second and, since both gases have roughly the same heat capacity of 29 kJ/K per kilomole, the heat removed is

$$P_{gases} = 1.56 \times 10^{-4} \times 29 \times 10^3 \times 60 = 271 \text{ W}.$$

In all probability, the correct amount is somewhere in between, but precision is not crucial because either amount is small compared with the total of 8230 W that has to be removed.

The heat to be removed by the coolant in the heat exchanger is either  $8230 - 470 = 7760$  W or  $8230 - 271 = 7959$  W. To be on the safe side, let's use the larger.

## Solution of Problem 10.2

The temperature rise of the cooling water in the heat exchanger is  $80 - 25 = 55$  K. With a heat capacity of 4,180 J/K per  $\text{m}^3$ , the coolant water flow must be

$$\dot{V} = \frac{7959 \times 3600}{4,180,000 \times 55} = 0.124 \quad \text{m}^3/\text{hr}.$$

Coolant water flow is a paltry 124 liters/hr.

**d. A consultant was called in and he improved catalysis in the anode reducing the operating voltage (at 20 kA) to 1.475 V. The cooling water can now be shut off. What is the new operating temperature?**

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The cooling water requirement is so small that it suggests that some slight improvement in the efficiency of the electrolyzer will allow dispensing with the cooling system.

After the changes, the electrolyzer operates with 1.475 V. This is in the endothermic regimen—heat is absorbed by the equipment, rather than shed by it. The amount of heat absorbed is

$$(1.484 - 1.475) \times 20,000 = 180 \quad \text{W}.$$

Again, we used 1.484 V. In this case, because we are taking the small difference between two numbers, the results may vary widely if a slightly different voltage is used.

Since the cell is completely heat insulated, the only heat introduction mechanism is the feed water that enters at 25 C. It flows at a rate of 6.71 kg/hour or 0.00186 kg/s.

To deliver 180 W to the cell, it must cool down by

$$\Delta T = \frac{180}{4180 \times 0.00186} = 23.2 \quad \text{K}.$$

The new operating temperature is  $25 - 23.2 = 1.8$  C.

The new operating temperature is 2 C.

## Solution of Problem    10.2



**Prob 10.3** Consider an ideal water electrolyzer installed at sea level and an ideal hydrogen/oxygen fuel cell installed 1000 m higher up.

The oxygen and the hydrogen produced electrolytically rise through a pipe and feed the fuel cell. Water is produced by the latter and flows down another pipe turning a turbine that drives as electric generator. The turbine/generator combination has 100% efficiency.

Here is a simple argument:

Since both electrolyzer and fuel cell are ideal (reversible), the electric energy generated by the fuel cell should be exactly the energy needed by the electrolyzer. But, there is some energy,  $W$ , generated by the flowing product water and this constitutes a net “profit”.

Clearly,

1. we have finally invented a perpetual motion machine, or
2. we are extracting energy from some non-obvious source, or
3. there is a flaw in the argument.

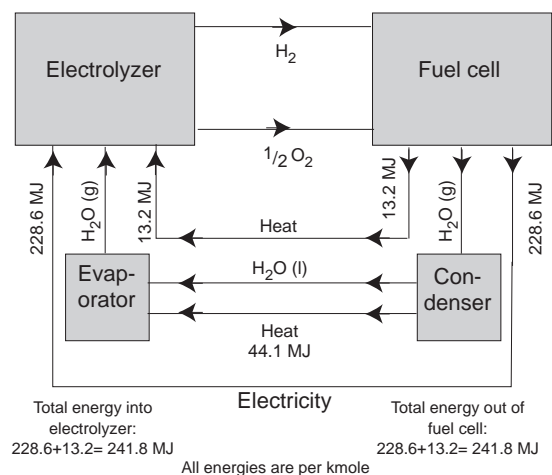
If you believe (1.), you are in trouble. It must be either (2.) or (3.). If it is (2.), describe the hidden source and demonstrate that it delivers precisely  $W$  units of energy. If (3.), explain what is wrong with the argument and demonstrate that  $W$  plus the energy delivered by the fuel cell is exactly equal to the energy required by the electrolyzer. Assume that the temperature of the electrolyzer is equal to that of the fuel cell.

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Although this was not asked, it is of interest to think of the configuration of the experiment which, clearly, cannot be realized because, among other things, it involves a lot of reversible processes. A fuel cell will produce gaseous water (it may, immediately condense or it may be exhausted as vapor). So, to have complete symmetry, the electrolyzer must use water vapor as well (difficult to implement if the temperature is 298 K). In other to have water driving a turbine, it is better to use a liquid. Thus there is, as shown in the figure, a condenser on top of the hill, a water pipe and a turbine (not shown) and then an evaporator. The heat from the condenser is used to evaporate the water—another unimplementable feature.

Assume that the electrolyzer operates with the output gases, both, at the same pressure,  $p_0$ , and at the temperature,  $T_0$ . Then, because the fuel cell is at a higher elevation, the two gases at its input will be at lower pressure,  $p_{O_2}$  and  $p_{H_2}$ , respectively. assume further that the temperature at the fuel cell is the same as at the electrolyzer.

## Solution of Problem 10.3



The pressure of a stratified gas in a gravitational field varies with height as<sup>†</sup>

$$p = p_0 \exp \left( -\frac{mg}{kT} \Delta h \right),$$

where  $\Delta h$ . Hence,

$$\frac{p_{H_2}}{p_0} = \exp \left( -m_{H_2} \frac{g}{kT_0} \Delta h \right),$$

and

$$\frac{p_{O_2}}{p_0} = \exp \left( -m_{O_2} \frac{g}{kT_0} \Delta h \right).$$

Owing to the pressure change, the free energies of the gases are altered by an amount equal to the energy of isothermal compression and the free energy change owing to the fuel cell reaction is:

$$\begin{aligned} \Delta G &= \Delta G_0 + RT_0 \ln \frac{p_{H_2}}{p_0} + \frac{1}{2} RT_0 \ln \frac{p_{O_2}}{p_0} \\ &= \Delta G_0 + RT_0 \ln \exp \left( -m_{H_2} \frac{g}{kT_0} \Delta h \right) + \frac{1}{2} RT_0 \ln \exp \left( -m_{O_2} \frac{g}{kT_0} \Delta h \right) \\ &= \Delta G_0 - RT_0 \frac{g}{kT_0} \Delta h \left[ (m_{H_2}) + \frac{1}{2} (m_{O_2}) \right] \\ &= \Delta G_0 - gN_0 m_{H_2O} \Delta h, \end{aligned}$$

because  $R = N_0 k$ .

Thus, the difference between electric energy used by the electrolyzer and that generated by the fuel cell is precisely the energy,  $gN_0 m_{H_2O} \Delta h$ , of the water coming down from the fuel cell site to the electrolyzer. The overall energy balance of the system is zero, as required by the first law of thermodynamics.

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<sup>†</sup> This is another example of Boltzmann's equation. See the appendix of the Textbook.

## Solution of Problem 10.3

**Prob 10.4** Hydrogen, to be produced electrolytically, is needed at 40 MPa and 25 C. Two possibilities must be considered by the engineers who are designing the plant:

- Produce hydrogen at 0.1 MPa and then compress it mechanically to 40 MPa.
- Pressurize the electrolyzer to 37 MPa and remove the hydrogen at 40 MPa. This assumes that the internal pressure difference between the oxygen and the hydrogen side is 3 MPa and that the oxygen is produced at the environmental pressure of the electrolyzer.

When operating at 0.1 MPa, the electrolyzer efficiency is 85%. However, when pressurized, its efficiency falls to 80%. The mechanical compressor has 65% efficiency.

- How much energy is needed to produce 1 ton of hydrogen in each case? Calculate the energy required to supply the feed water (only the energy necessary to force the water into the pressurized environment).

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a1. Mechanical compression of the hydrogen.

To produce 1 kilomole of  $H_2$  at RTP, the electrolyzer requires

$$W_{Electrolyzer} = \underbrace{285.9 \times 10^6}_{J/[kmole\ H_2]} \times \underbrace{\frac{1}{0.85}}_{\text{electrolyzer efficiency}} = 336.4 \times 10^6 \quad J [kmole (H_2)]^{-1}.$$

To compress one kilomole of this isothermally from 1 to 400 atmospheres, one needs, ideally (at 298 K):

$$W_{COMPR.}^{IDEAL} = RT \ln \frac{p}{p_0} = 8314 \times 298 \ln \frac{400}{1} = 14.8 \times 10^6 \quad J [kmole (H_2)]^{-1}.$$

Due to its 65% efficiency, the input energy to the compressor must be

$$W_{COMPR} = \frac{14.8 \times 10^6}{0.65} = 22.8 \times 10^6 \quad J [kmole (H_2)]^{-1}.$$

The total energy necessary to deliver hydrogen at 400 atmospheres is

$$W_{T Mech} = (336.4 + 22.8) = 359.2 \quad MJ [kmole (H_2)]^{-1}.$$

Molecular mass of hydrogen is 2 kg/kmole, hence, 1 ton of hydrogen is 500 kmoles. The energy to produce this is  $359.2 \times 10^6 \times 500 = 180 \times 10^9$  J.

180 GJ are needed to produce 1 ton of hydrogen.

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## Solution of Problem 10.4

a2. High pressure electrolysis.

To produce 1 kilomole of  $H_2$  at 400 atmos and 298 K, the electrolyzer requires energy,  $W_{Electrolyzer_{RTP}}$ , to separate the water into its components at RTP plus the energy,  $W_{Compress_{H_2}}$ , to compress the hydrogen gas from 1 to 400 atmospheres plus the energy,  $W_{Compress_{O_2}}$ , to compress the oxygen from 1 to 370 atmospheres (see problem statement). When operating at high pressure, the efficiency falls from the original 85% to 80%.

$$\begin{aligned} W_{Electrolyzer_{RTP}} &= \underbrace{285.9 \times 10^6}_{J/[kmole \ H_2]} \times \underbrace{\frac{1}{0.80}}_{\text{electrolyzer efficiency}} \\ &= 357.4 \times 10^6 \quad J \ [kmole \ (H_2)]^{-1}, \end{aligned} \quad (1)$$

$$\begin{aligned} W_{Compress_{H_2}} &= \frac{1}{\eta} RT \ln \frac{p}{p_0} = \frac{1}{0.80} 8314 \times 298 \ln \frac{400}{1} \\ &= 18.6 \times 10^6 \quad J \ [kmole \ (H_2)]^{-1}. \end{aligned} \quad (2)$$

$$\begin{aligned} W_{Compress_{O_2}} &= \frac{1}{2} \frac{1}{\eta} RT \ln \frac{p}{p_0} = \frac{1}{2} \times \frac{1}{0.80} \times 8314 \times 298 \ln \frac{370}{1} \\ &= 9.1 \times 10^6 \quad J \ [kmole \ (H_2)]^{-1}. \end{aligned} \quad (3)$$

where the factor,  $\frac{1}{2}$ , corresponds to there being  $\frac{1}{2}$  kilomole of oxygen for each kilomole of hydrogen.

Thus, the total energy to produce the two gases is

$$W_{TElectrolytic} = 357.4 + 18.6 + 9.1 = 385.1 \quad MJ \ [kmole \ (H_2)]^{-1}. \quad (4)$$

To this, we have to add the energy to force the water into the electrolyzer against the 370 atmosphere pressure in the device.

Each kilomole of hydrogen requires 1 kilomole of water or 18 kg of water. The density of the liquid is 1000 kg/m<sup>3</sup>, hence we need 0.018 m<sup>3</sup> of water per kilomole of hydrogen. The energy to feed this water into the electrolyzer is

$$W_{H_2O} = p\Delta V = 370 \times 10^5 \times 0.018 = 0.67 \times 10^6 \quad J \ [kmole \ (H_2)]^{-1}.$$

This is a negligible amount of energy compared with what is needed to produce and compress the gases. The energy per kilomole of hydrogen is then 385.8 MJ and per ton of hydrogen is  $385.8 \times 500 = 192,900$  MJ.

The energy to produce and compress hydrogen electrolytically is 193 GJ per ton of hydrogen.

## Solution of Problem 10.4

This is slightly more than that required by the mechanical compression scheme. The electrolytic compression may require less maintenance. The deciding factor may be a comparison of the capital investment of the two systems.

One may also consider the possibility of expanding the oxygen in a turbine to recover the energy used in compressing it.

More importantly, the electrolytic compression yields pure oxygen as a by-product with substantial commercial value.

- b. The high pressure oxygen can be expanded to 0.1 MPa through a turbine. How much energy can you recover if you have a 100% efficient turbo-generator? What is the temperature of the exhaust oxygen assuming an adiabatic (completely insulated) turbo-generator? Assume the oxygen does not condense.**

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The turbine expands the oxygen adiabatically. From the first law of thermodynamics,

$$\Delta Q = \Delta U - \Delta W = 0 \quad (5)$$

because in an adiabatic process no heat is exchanged with the environment. Consequently,

$$\Delta W = \Delta U = \int_{T_0}^T c_v dt = c_v \Delta T. \quad (6)$$

The last equality is valid if  $c_v$  is independent of the temperature.

We must find  $\Delta T$ . Under adiabatic conditions,  $pV^\gamma = \text{constant}$  and for all ideal gases,  $pV = RT$  (per kilomole). Thus,

$$\begin{aligned} V^\gamma &= \frac{(RT)^\gamma}{p^\gamma}, \\ pV^\gamma &= \text{constant} = p^{1-\gamma}(RT)^\gamma, \\ p^{\frac{1-\gamma}{\gamma}}T &= \text{constant} = p_0^{\frac{1-\gamma}{\gamma}}T_0. \\ T &= T_0 \left( \frac{p_0}{p} \right)^{\frac{1-\gamma}{\gamma}}. \end{aligned} \quad (7)$$

We need the value of  $\gamma$  for oxygen. From Table 10.5 we see that it is 1.354 at 300 K and 1.386 at 100 K. As a guess, we can take 1.37 as a representative value. If so, we get  $T \approx 60$  K. The corresponding  $\Delta T$  is 238.

$c_p$ , as read off from Table 10.5 is, for the temperature range of interest, about 30 kJ K<sup>-1</sup>kmole<sup>-1</sup> and  $c_v = c_p/\gamma \approx 22$  kJ K<sup>-1</sup>kmole<sup>-1</sup>.

The work done by the turbine is

$$\Delta W = 22,000 \times 238 = 5.2 \quad \text{MJ/kmole.} \quad (8)$$

## Solution of Problem 10.4

**Prob 10.5** An electrolyzer consists of 100 cells, each with 1 m<sup>2</sup> of effective area. The efficiency of each cell is given by

$$\eta = 1.205 + bJ,$$

where  $J$  is the current density in A/m<sup>2</sup>.

When  $J = 1000$  A/m<sup>2</sup>, the voltage required by each cell is 1.310 V.

The electrolyzer is installed in a cubical room (3 m edge) whose walls, floor and ceiling conduct heat at a rate of 50 W/m<sup>2</sup> per kelvin of temperature difference. No other source or sink of heat is in the room. Outside temperature is 30 C.

When a current of 1000 A is forced through the cells,

a. How many kg of H<sub>2</sub> are produced per day? .....

$$1000 \text{ A} = 1000 \text{ coulombs/s} = \frac{1000}{1.60 \times 10^{-19}} = 6.24 \times 10^{21} \text{ electrons/s.}$$

2 electrons are required to produce 1 molecule of H<sub>2</sub>, hence, the hydrogen production rate is

$$\dot{N}_{H_2} = \frac{1}{2} \frac{6.24 \times 10^{21}}{6.02 \times 10^{26}} = 5.18 \times 10^{-6} \text{ kmol(H}_2\text{) /second,}$$

$$\dot{N}_{H_2} = 5.18 \times 10^{-6} \times 86,400 = 0.448 \text{ kmol(H}_2\text{) /day} \rightarrow 0.90 \text{ kg(H}_2\text{) /day.}$$

This is the production rate per cell, but there are 100 cells, hence,

Daily hydrogen production is 90 kg.

b. How many kg of O<sub>2</sub> are produced per day? .....

For each kilomole of hydrogen, half a kilomole of oxygen is produced. Since the molecular mass of oxygen is 16 times that of hydrogen, the gases are produced at a 8:1 ratio.

Daily oxygen production is 720 kg

c. How many kg of H<sub>2</sub>O are consumed per day? .....

The amount of water consumed must be the sum of the amount of hydrogen plus oxygen produced:

$$\dot{N}_{H_2O} = 0.9 + 7.2 = 8.1 \text{ kg(H}_2\text{O) /day.}$$

Solution of Problem 10.5

Daily water consumption is 810 kg.

**d. What is the equilibrium temperature of the room?**

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 The problem statement says that when  $J=1000 \text{ A/m}^2$ , the voltage across the electrolyzer is 1.310 V. Consequently, the amount of heat rejected by the electrolyzer is

$$W_{HEAT} = (1.310 - 1.482) \times 1000 = -172 \text{ W/m}^2.$$

This actually means that 172 W of heat are absorbed by each cell.

The 100 cells will reject a total of 17,200 W.

Total wall + ceiling + floor area of the room is  $6 \times 3^2 = 54 \text{ m}^2$ . The different faces of the room (walls, etc) must conduct  $17,200/54 = 318 \text{ W/m}^2$  of heat. Since the heat conductivity is 50 W/m<sup>2</sup> per kelvin,

$$318 = 50\Delta T,$$

$$\Delta T = 6.4 \text{ K}.$$

With an outside temperature of 30 C, the room will cool down to  $30 - 6.4 = 23.6 \text{ C}$ .

The room will cool down to 23.6 C

**e. What current causes the room to reach the lowest possible temperature?**

.....  
 The efficiency of an electrolyzer can be expressed in terms of the voltage necessary for its operation;

$$\eta = \frac{1.482}{V}. \quad (1)$$

For the present example,

$$\eta = 1.205 + bJ = \frac{1.482}{V},$$

which yields a value of  $b = -7.37 \times 10^{-5}$  when the values,  $J = 1000 \text{ A/m}^2$  and  $V = 1.310 \text{ V}$ , are introduced.

Thus,

$$\eta = 1.205 - 7.37 \times 10^{-5} J. \quad (2)$$

Combining Equations 1 and 2,

$$V = \frac{1.482}{1.205 - 7.37 \times 10^{-6} J} = \frac{1.230}{1 - 61.16 \times 10^{-6} J}. \quad (3)$$

## Solution of Problem 10.5

Using a binomial approximation we can write this in the more familiar form of

$$V \approx 1.230(1 + 61.16 \times 10^{-6}J) = 1.230 + 75.2 \times 10^{-6}J. \quad (4)$$

At  $J = 1000 \text{ A/m}^2$ ,  $V = 1.310 \text{ V}$ . This result was obtained from Equation 3 which is more accurate than Equation 4. The latter would have yielded  $V = 1.305 \text{ V}$ .

$$\begin{aligned} W_{HEAT} &= (1.482 - V)J = \left(1.482 - \frac{1.230}{1 - 61.16 \times 10^{-6}J}\right)J \\ &= 1.482J - \frac{1.23J}{1 - 61.16 \times 10^{-6}J} \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{dW_{HEAT}}{dJ} &= 1.482 - \frac{1.23}{1 - 61.16 \times 10^{-6}J} - \frac{61.16 \times 10^{-6} \times 1.23J}{(1 - 61.16 \times 10^{-6}J)^2} = 0, \\ J^2 - 32700J + 45.46 \times 10^6 &= 0, \\ J &= \frac{32700 \pm \sqrt{32700^2 - 4 \times 45.46 \times 10^6}}{2} \\ &= \frac{32700 \pm 29790}{2} = \begin{cases} 1457 \text{ A/m}^2 \\ 31250 \text{ A/m}^2 \end{cases} \end{aligned}$$

We observe that with  $J = 1457 \text{ A/m}^2$ , the electrolyzer voltage is  $1.352 \text{ V}$ , i.e., a voltage smaller than  $1.482$ , hence the electrolyzer still acts as a heat pump and cools the room. To obtain larger current densities, it is necessary to apply progressively larger voltages and, soon, the applied voltage will exceed  $1.482 \text{ V}$  and the electrolyzer will heat the room instead of cooling it as required by the problem statement. For instance, with  $J = 10,000 \text{ A/m}^2$ , Equation 3 predicts a voltage of  $3.167 \text{ V}$ .

At high currents, Equation 3 breaks down; it predicts infinite voltage for  $J = 16,350 \text{ A/m}^2$ . Thus, the only acceptable answer is

Maximum room cooling occurs when the current density is  $1457 \text{ A/m}^2$ .

## Solution of Problem 10.5



**Prob 10.6** A water electrolyzer operating at RTP requires 1.83 V to produce 1 metric ton of hydrogen per day when operating continuously.

**a. What current does it draw?**

1 metric ton of hydrogen per day corresponds to 500 kilomoles of hydrogen per day or  $5.8 \times 10^{-3}$  kilomoles of hydrogen per second. Since it takes 2 kilomoles of electrons to free 1 kilomole of  $H_2$ , one ton of hydrogen per day requires a flow of  $11.6 \times 10^{-3}$  kilomoles of electrons per second or  $11.6 \times 10^{-3} \times 6.02 \times 10^{26} = 7.0 \times 10^{24}$  electrons per second. This corresponds to a current of  $7.0 \times 10^{24} \times 1.6 \times 10^{-19} = 1.12 \times 10^6$  amperes.

To produce 1000 kg of hydrogen per day, a current of 1.12 MA (megamperes) is needed.

A better design would call for a large number of cells in series so as to reduce the required current. Say, 100 cells operating under 183 V and drawing 11.2 kA.

---

**b. How many  $m^3$  of water does it use per day?**

The electrolyzer will need 1 kilomole of feed water for every kilomole of hydrogen produced. This would amount to 500 kilomoles of water or 9000 kg or  $9 m^3$  of water per day.

Daily feed water consumption is 9 cubic meters.

---

**c. How many MJ of heat does it either reject or absorb per day (state which)?**

The electrolyzer (per cell) voltage exceeds the 1.48 V thermal break-even voltage. Hence, heat will be released. The overvoltage is  $1.83 - 1.48 = 0.35$  V. The heat loss is  $0.35 \text{ V} \times 1.12 \times 10^6 \text{ A}$  or  $3.9 \times 10^5 \text{ W}$ . The heat energy generated throughout a 24-hour period is  $3.9 \times 10^5 \times 86,400 = 33.9 \times 10^9 \text{ J/day}$ .

Daily heat rejection is 33,900 MJ or 33.9 GJ.

---

## Solution of Problem 10.6

**Prob 10.7** We want to estimate the performance of a system for the production of ammonia in geographically dispersed plants. Input energy is to be electrical.

The agricultural plot to be served by each ammonia plant is to be 20 by 20 km in effective cultivated area.

Nitrogen fertilization is to be intensive: 40 kg of ammonia per hectare per year (1 ha= 10,000 m<sup>2</sup>).

The electrolyzers will operate at a current density that results in 85% overall practical efficiency (at RTP). Current efficiency is 100%.

- a. Assuming that the plants operate 24 hours per day, how many tons (1000 kg) must each plant produce per day?

.....

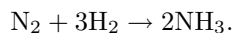
The area to be fertilized by each ammonia plant is 20 by 20 km or 400 million square meters. Since one hectare is 10,000 m<sup>2</sup>, this corresponds to 40,000 hectares. Ammonia consumption is 40 kg per hectare per year or  $1.6 \times 10^6$  kg (NH<sub>3</sub>) per year or 4400 kg (NH<sub>3</sub>) per day.

Daily ammonia production must be 4.4 tons.
--

- 
- b. How much power does each electrolyzer demand?

.....

The ammonia producing reaction is



Consequently, for each kilomole of ammonia (17 kg), 1.5 kilomoles (3 kg) of hydrogen are required. For 4400 kg (258 kmole) of ammonia, 770 kg (387 kmole) of hydrogen are required. This is the daily rate. Per second, 0.009 kg (0.0045 kmole) of H<sub>2</sub> are needed.

The efficiency of a practical electrolyzer is defined as 100% when the electric energy needed is exactly equal to the enthalpy change of water dissociation, i.e., when 142 MJ of electricity are used to produce 1 kg of hydrogen.

At 142 MJ/kg, the power used would be 1.3 MW, however, the efficiency of the plant is only 85%. This raises the input power to 1.54 MW.

The electric power required is 1.54 MW plus some additional overhead power.
--

---

## Solution of Problem 10.7

**c. What is the voltage of each electrolyzer cell?**

.....  
The efficiency of the electrolyzer is

$$\eta = \frac{1.48}{V},$$

hence,  $V = 1.48/0.85 = 1.74$  V.

Each electrolyzer cell has 1.74 V across it.

**d. What is the current through each cell?**

.....  
If a single cell were used, the current would be  $1.54 \times 10^6 / 1.74 = 885,000$  A. A better design would use 100 series-connected cells drawing a current of 8.85 kA.

If a single cell is used, the current is 885 kA.  
Better: Use 100 cells with a current of 8.85 A.

**e. Assume that instead of delivering the gases at 1 atmosphere, the electrolyzer is required to deliver them at 400 atmospheres. Clearly, additional electric power will be needed. Assume that this additional power is exactly the power for isothermal compression of the gases. How much is this additional power?**

.....  
When the two gases are delivered at 400 atmospheres (400 times the previous pressure), then there is an additional energy requirement to compress the gases isothermally:

$$W_{ox} = \frac{1}{2}RT \ln 400 = \frac{1}{2} \times 8314 \times 298 \times \ln 400 = 7.4 \times 10^6 \text{ MJ per kmole of H}_2.$$

$$W_h = RT \ln 400 = 8314 \times 298 \times \ln 400 = 14.8 \times 10^6 \text{ MJ per kmole of H}_2.$$

The additional energy is 22.2 MJ/kmole of H<sub>2</sub> or 11.1 MJ/kg of H<sub>2</sub>.

The total energy required is  $(1.41 + 11)/0.85 = 180$  MJ per kg of H<sub>2</sub>.  
The power required is  $180 \times 10^6 \times 0.009 = 1.62$  MW.

For gas delivery at 400 atmospheres,  
15mm the power consumption is 1.62 MW.

**f. In the traditional ammonia process, 80% of the cost of production is the cost of energy. The price of ammonia in the****Solution of Problem 10.7**

international market is \$200/ton. Thus, \$40/ton cover all the non-energy related costs. How much can you afford to pay for 1 kWh and still make a 10% profit? Remember that the \$40/ton remain unchanged.

.....  
In the traditional ammonia process, the energy cost per ton of ammonia is  $0.8 \times \$200 = \$160$ . This means that the rest of the cost is \$40. To make a 10% profit (when you charge the usual \$200/ton), your total cost must be \$182/ton and, since the non-energy related cost is still \$40/ton, your energy cost must not exceed \$142/ton.

To produce 1 ton of ammonia, the electrolyzer must operate 1/4,4 days or 20,000 seconds. At 1.62 MJ/s, the energy used is 32 GJ or 8.9 MWh. You can afford to pay \$142 for 8.9 MWh of electricity or 16 mils<sup>†</sup> per kWh.

To make 10% or more profit,  
the electricity must cost 16 mils/kWh or less.

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<sup>†</sup> The cost of electricity is often quoted in mils/kWh. Mil stands for millidollar, or 0.1 cents.

## Solution of Problem 10.7

**Prob 10.8** A hydrogen producer has a battery of 100 cells connected in series. A  $v$ - $i$  test shows that a current of 35.6 A must be driven into any of the cells to achieve a 1.482 V potential drop across it. As the current is decreased, the voltage also decreases and, as the current approaches 0, the voltage approaches 1.376 V.

A production rate of 1 liter ( $0.001 \text{ m}^3$ ) of  $\text{H}_2$  per second at RTP is required. What voltage must be applied to the battery?

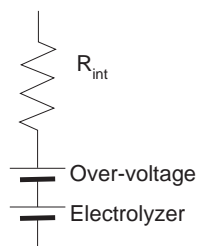
Model each cell as an ideal electrolyzer in series with an opposing voltage generator and a resistance of constant value (independent of the current).

.....  
The production rate depends solely on the current through the cell.

Each cell has to produce 1/100 liters of  $\text{H}_2$  per second. 0.001 liters of an ideal gas at RTP corresponds to a quantity

$$\mu = \frac{pV}{RT} = \frac{10^5 \times 0.00001}{8314 \times 298} = 40 \times 10^{-8} \quad \text{kmole}$$

At 2 kilomoles of electrons per kilomole of  $\text{H}_2$ , the rate of electron flow must be  $80 \times 10^{-8}$  kmoles/s or  $80 \times 10^{-8} \times 6 \times 10^{26} = 48.6 \times 10^{19}$  electrons/second or  $48.6 \times 10^{19} \times 1.6 \times 10^{-19} = 78 \text{ A}$ .



The electrolyzer is to be modeled as an ideal device in series with an *over-voltage* and a resistance. At RTP, the ideal electrolyzer requires 1.231 V to conduct any current. The electrolyzer in this problem requires 1.376 V to start conducting. Thus, in the model, the over-voltage is  $1.376 - 1.231 = 0.145 \text{ V}$ . The equation describing the voltage versus current behavior of the device is

$$V = 1.376 + IR_{int}.$$

When a current of 35.6 A circulates through the electrolyzer, the terminal voltage is 1.482 V:

$$1.482 = 1.376 + 35.6R_{int},$$

$$R_{int} = 0.003 \quad \text{ohms.}$$

The voltage that must be applied to each cell to force 78 amperes through it is

$$V = 1.376 + 78 \times 0.003 = 1.610 \quad \text{V.}$$

The voltage applied to the battery is 161 V.

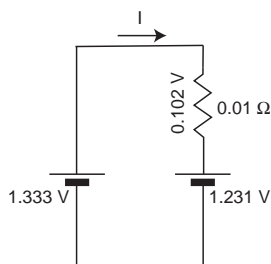
To produce 1 liter of hydrogen per second (at RTP),  
161 V must be applied to the battery.

## Solution of Problem 10.8

**Prob 10.9** Consider an ideal water electrolyzer in series with a  $0.01\ \Omega$  resistance. The gas outlets are connected to small closed vessels of equal volume so that when the device operates, gas pressure builds up. Initially, both the oxygen pressure and the hydrogen pressure are 1 atmosphere. The electrolyzer operates at 298 K.

A 1.333 V constant-voltage power supply is connected to the electrolyzer, in series with the  $0.01\ \Omega$  resistor.

a. What is the initial current?



Reversible water electrolyzers, at RTP, require 1.231 V. Since, 1.333 V are applied, the voltage drop across the resistor must be  $1.333 - 1.231 = 0.102$  V. The current that causes this voltage drop across an 1-ohm resistor is

$$I = \frac{V}{R} = \frac{0.102}{0.01} = 10.2 \quad \text{A.}$$

The initial current is 10.2 A.

b. As time goes on, the pressures in the gas containers rise. Assuming these containers do not rupture, what is the maximum hydrogen pressure that the system will reach?

As the pressure rises, so will the energy (and, consequently, the reversible voltage) required to perform the electrolysis.

The energy increment per kilomole of hydrogen is

$$\Delta W = RT \ln \frac{p_{Hy}}{p_{Hy_0}} + 0.5RT \ln \frac{p_{Ox}}{p_{Ox_0}} = RT \ln \left( \frac{p_{Hy}}{p_{Hy_0}} \frac{p_{Ox}^{0.5}}{p_{Ox_0}^{0.5}} \right).$$

Since the number of kilomoles of oxygen produced is half of that of hydrogen, the oxygen pressure built up will be (very nearly, if the collecting vessels are small enough) half of that of the hydrogen:  $p_{Ox} = 0.5p_{Hy}$ .

According to the statement of the problem,  $p_{Ox_0} = p_{Hy_0} = 1$  atmos:

$$\Delta W = 8314 \times 298 \ln \left( \frac{p_{Hy}^{1.5}}{\sqrt{2}} \right) = 2.478 \times 10^6 \ln \left( \frac{p_{Hy}^{1.5}}{\sqrt{2}} \right)$$

Expressing this excess energy in terms of excess voltage,

$$\Delta V = \frac{\Delta W}{n_e q N_0} = 12.84 \times 10^{-3} \ln \left( \frac{p_{Hy}^{1.5}}{\sqrt{2}} \right) = 0.102 \quad \text{V.}$$

## Solution of Problem 10.9

When the reversible voltage is equal to the voltage available from the power supply, current no longer flows and the production of gases stops. The pressure ceases to rise. Thus, the maximum hydrogen pressure is that given by the equality above. Solving for  $p_{Hy}$ , one obtains

$$p_{Hy} = 250 \quad \text{atmos.}$$

The hydrogen pressure will reach 250 atmospheres.

---

Solution of Problem    10.9

**Prob 10.10** A spherical balloon is filled with hydrogen until the internal pressure equals that of the surrounding air. The bag is made of a material that can expand or contract but contributes negligibly to the pressure of the gas. The temperature of the hydrogen is equal to that of the air. The balloon, when empty, weighs 32 kg. When the air pressure is exactly one atmosphere and its temperature is 0 C, the balloon has a diameter of 10.0 m.

- a. What is its net lifting force? How does the lift force depend on the external pressure and temperature?

At  $p = 1$  atmosphere and  $T = 273$  K, the volume,  $V$ , of the balloon is

$$V = \frac{4}{3}\pi r^3 = 1.25 \times 3.141 \times 5^3 = 523.6 \quad \text{m}^3.$$

The volume of one kilomole of a gas is

$$V = \frac{RT}{p}.$$

Hence, the density of hydrogen is

$$\delta_{H_2} = \frac{2 \text{ kg kmole}}{\text{kmole } V} = \frac{2p}{RT}.$$

The mass of hydrogen in the balloon is

$$M_{H_2} = 523.6 \frac{2p}{RT} = \frac{1047 \times 1.0133 \times 10^5}{8314 \times 273.15} = 46.7 \quad \text{kg}.$$

Note that  $M_{H_2}$  is independent of  $p$  and  $T$ .

The density of air (20% oxygen, 80% nitrogen) is

$$\delta_{air} = \frac{0.2 \times 32 + 0.8 \times 28 \text{ kg kmole}}{\text{kmole } V} = \frac{28.8p}{RT}.$$

The volume of the displaced air is  $523.6 \frac{p_0}{p} \frac{T}{T_0}$ , where  $p_0$  is 1 atmosphere and  $T_0 = 273.2$  K.

The mass of the displaced air is

$$M_{air} = 523.6 \frac{p_0}{p} \frac{T}{T_0} \frac{28.8p}{RT} = \frac{15080p_0}{RT_0} = 672.9 \quad \text{kg}.$$

Hence, the mass of the displaced air is also independent of  $p$  and  $T$ . This means that the lift force is independent of pressure and temperature.

The lift force is

$$F_{lift} = M_{air} - M_{H_2} - M_{balloon} = 672.9 - 46.7 - 32 = 594.2 \quad \text{kg}.$$

The balloon can lift 594 kg independently of air pressure and temperature, hence, independently of height.

## Solution of Problem 10.10



- b. To fill the balloon above, a water electrolyzing plant is employed. The plant consists of 100 cells, each operated a 2000 A and 1.92 V. How long must this plant operate to produce the required amount of hydrogen?

.....  
 The volume of hydrogen needed is  $523.6 \text{ m}^3$  at STP. This corresponds to

$$\mu = \frac{pV}{RT} = \frac{523.6 \times 1.0133 \times 10^5}{8314 \times 273.2} = 23.4 \quad \text{kmole.}$$

For each kilomole of  $\text{H}_2$ , 2 kilomoles of electrons are needed for the electrolysis. Hence the total number of electrons needed is 46.8 kilomoles. The total charge is  $46.8 \times 6.02 \times 10^{26} \times 1.6 \times 10^{-19} = 4.5 \times 10^9$  coulombs.

The current through each cell is 2000 coulombs/sec and each cell must produce 1/100 of the required hydrogen. Then the time required for the electrolysis is

$$t = \frac{4.5 \times 10^9}{100 \times 2000} = 22,500 \text{ s or } 6.25 \text{ h or } 6:15 \text{ h.}$$

To produce the required amount of hydrogen, the plant must operate 6:15 hours.

- c. How much feed water is used per second (express this in liters per second)?

.....  
 For each kilomole of hydrogen produced, 1 kilomole of water is consumed. For 23.4 kilomoles of hydrogen, the water consumption is  $23.4 \times 18 = 421 \text{ kg}$  of water. This is 421 liters in 6.25 hours or 0.0187 liters per second.

The water consumption rate is 18.7 milliliters/second.

- d. What is the rate of heat production by the plant?

.....  
 The voltage across a cell that neither absorbs nor produces heat is 1.48 V. Thus, the heat produced per cell is  $(1.92 - 1.48) \times 2000 = 880 \text{ W}$ . The heat generated by the whole plant is 88 kW.

The plant dissipates 88 kW of heat.

## Solution of Problem 10.10

**Prob 10.11** A battery of 12 water electrolyzers connected in series (so that the same current flows through each unit) operates in a room maintained at 298 K. The product gases are withdrawn under a pressure of 1 atmosphere. A voltage of 17.784 V is applied and the resultant current is 1200 A.

**a. Calculate the production rate of hydrogen in kg/day.**

.....  
The production rate depends only on the current. Each unit will produce

$$\begin{aligned}\dot{N}_{H_2} &= \frac{I}{2qN_0} = \frac{1200}{2 \times 1.60 \times 10^{-19} \times 6.02 \times 10^{-26}} \\ &= 6.22 \times 10^{-6} \text{ kmol (H}_2\text{)/s.}\end{aligned}$$

Since there are 86400 seconds in a day and each kilomole of hydrogen masses 2 kg and there are 12 units in the battery, the production rate is

$$86,400 \times 2 \times 12 \times 6.22 \times 10^{-6} = 12.9 \text{ kg/day.}$$

The battery produces 12.9 kg of hydrogen per day.
---

---

**b. Calculate the water consumption in liters/day.**

.....  
For each kilogram of H<sub>2</sub>, 9 kilograms of water are needed. Hence the water consumption rate is  $9 \times 12.9 = 116$  kg/day or 116 liters/day.

The water consumption rate is 116 liters/day.
---

---

**c. Calculate the operating temperature of the electrolyzers.**

.....  
The voltage across each unit of the battery is  $17.784/12 = 1.482$  V. An electrolyzer operating under such a voltage neither heats up nor cools down, hence, it operates at the temperature of the environment.

The electrolyzer operates at 298 kelvins.
---

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## Solution of Problem 10.11

**Prob 10.12** How much power does an ideal electrolyzer operating at 298.2 K require to produce 1 kg of hydrogen per hour at a pressure of 400 atmospheres? The oxygen is produced at 370 atmospheres.

.....  
The input power of an ideal electrolyzer is

$$P_{in} = |\Delta G| \dot{N}. \quad (1)$$

1 kg/h of H<sub>2</sub> is 1/2 kmole/h =  $139 \times 10^{-6}$  kmole/s =  $\dot{N}$ . Hence

$$P_{in} = 139 \times 10^{-6} |\Delta G|.$$

At RTP,  $\Delta G = 237.2$  MJ/kmole. The energy necessary to compress isothermally 1 kmole of hydrogen to 400 atm plus 0.5 kmole of oxygen to 370 atm is

$$W_{compr.} = RT(\ln 400 + 0.5 \ln 370) = 22.2 \times 10^6 \text{ J/kmole (H)}_2. \quad (3)$$

The power required is

$$P_{in} = 259.4 \times 10^6 \times 139 \times 10^{-6} = 36,000 \text{ W}. \quad (4)$$

The power required is 36 kW.
------------------------------

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Solution of Problem 10.12

**Prob 10.13** You have been hired to run a hydrogen production plant. The fixed cost (amortization of the equipment and the buildings, salaries, taxes, etc.) amounts to  $c_F = \$2000/\text{day}$  regardless of how much hydrogen is produced.

The electrolyzer consists of  $N$  cells connected in series, each having the characteristic,

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

The utility will provide electric energy at a price,  $c$  (in  $\$/\text{kWh}$ ), that can vary from day to day, depending on availability.

- a. Each day you must adjust the hydrogen production rate,  $H_{\text{prod.rate}}$  (in  $\text{kg}/\text{day}$ ) so as to minimize the cost of the gas. To this end, you must develop a formula that tells you the optimal production rate as a function of  $c$ .

.....  
When operating at a current,  $I$ , the hydrogen production rate is

$$\dot{N} = \frac{N}{2qN_0}I \quad \text{kmoles (H}_2\text{)}/\text{s}.$$

Per day the rate is

$$\begin{aligned} H_{\text{prod.rate}} &= \frac{86400N}{2qN_0}I \quad \text{kmoles (H}_2\text{)}/\text{day} = \frac{86400}{1.6 \times 10^{-19} \times 6 \times 10^{26}}NI \\ &= 895.5 \times 10^{-6}NI \quad \text{kg (H}_2\text{)}/\text{day}. \end{aligned} \quad (1)$$

The required input power is

$$\begin{aligned} P_{in} &= (V_0 + R_{int}I)IN \quad \text{J/s} = \frac{86400}{3.6 \times 10^6}(V_0 + R_{int}I)IN \\ &= 24 \times 10^{-3}(V_0 + R_{int}I)IN \quad \text{kWh}/\text{day}. \end{aligned} \quad (2)$$

Since the cost of the kWh of electricity is  $c$  dollars, the cost of the required electricity (per day) is

$$c_E = 24 \times 10^{-3}(V_0 + R_{int}I)INc \quad \$/\text{day}. \quad (3)$$

The cost of the hydrogen produced is

$$c_H = c_F + c_E = 2000 + 24 \times 10^{-3}(V_0 + R_{int}I)INc \quad \$/\text{day}. \quad (4)$$

But, the production rate was given by Equation 1,

$$\begin{aligned} C_H &= \frac{c_H}{H_{\text{prod.rate}}} = \frac{c_F + c_E}{H_{\text{prod.rate}}} = \frac{2000 + 24 \times 10^{-3}(V_0 + R_{int}I)INc}{895.5 \times 10^{-6}NI} \\ &= \frac{2.233 \times 10^6}{NI} + 26.80V_0c + 26.80R_{int}Ic \quad \$/\text{kg}. \end{aligned}$$

## Solution of Problem 10.13

The current that minimizes  $C_H$ , can be found by

$$\frac{dC_H}{dI} = -\frac{2.233 \times 10^6/N}{I^2} + 26.80R_{int}c = 0,$$

from which

$$I = \sqrt{\frac{2.233 \times 10^6}{26.80R_{int}cN}} = 288.7 \sqrt{\frac{1}{R_{int}cN}} \quad (5)$$

Using this value of  $I$ , Equation 1 yields,

$$H_{prod.rate} = 0.2585N \sqrt{\frac{1}{R_{int}cN}} \quad \text{kg (H}_2\text{)/day.} \quad (6)$$

- 
- b. Calculate the hydrogen production rate that leads to the cheapest gas for the case in which there are 250 series connected cells each one having the characteristic**

$$V = 1.420 + 20 \times 10^{-6}I.$$

**Do this for the an electric energy cost of 2 cents per kWh.**

.....  
For the case under consideration,

$$N = 250,$$

$$R_{int} = 20 \times 10^{-6} \text{ Ohms},$$

$$c = 0.02 \text{ \$/kWh}.$$

Using Equation 6, one obtains

The hydrogen production rate is 6463 kg/day.

Incidentally, the current required for the above hydrogen production rate is

$$I = 288.7 \sqrt{\frac{1}{20 \times 10^{-3} \times 0.02 \times 250}} = 28,867 \quad \text{A.}$$


---

## Solution of Problem 10.13

**Prob 10.14** Consider the electrolyzer of Problem 10.13, operating at 20,000 A.

Calculate

1. The total voltage that must be applied.
2. The hydrogen production rate in kg (H<sub>2</sub>)/day.
3. The rate of water consumption in m<sup>3</sup>/day.
4. The heat power rejected.

.....  
The voltage that must be applied to the electrolyzer is

$$V = (1.420 + 20 \times 10^{-6} \times 20,000) \times 250 = 1.820 \times 250 = 455 \quad \text{V.}$$

At 20,000 A, the hydrogen production rate is

$$\begin{aligned} H_{\text{prod.rate}} &= \frac{20,000}{2qN_0} N = \frac{20,000}{2 \times 1.6 \times 10^{-19} \times 6 \times 10^{26}} \times 250 \\ &= 25.9 \times 10^{-3} \quad \text{kmole (H}_2\text{)/s} \quad \text{or} \\ &51.8 \times 10^{-3} \quad \text{kg (H}_2\text{)/s} \quad \text{or} \quad 4,478 \quad \text{kg (H}_2\text{)/day} \end{aligned}$$

The kilomoles of water consumption is the same as that of hydrogen production. The water molecule masses 9 times that of the hydrogen molecule, hence, the water consumption rate is

$$Water_{\text{cons.rate}} = 9 \times 4,478 = 40.3 \times 10^3 \quad \text{kg/day} \quad \text{or} \quad 40.3 \quad \text{m}^3 \text{ day.}$$

The heat power reject is

$$W_{\text{heat}} = 250 \times (1.820 - 1.482) \times 20,000 = 1.69 \times 10^6 \quad \text{W.}$$

Voltage required by the electrolyzer: 455 V.  
Hydrogen production: 4,478 kg/day.  
Water consumption: 40.3 cubic meters/day.  
Heat rejected: 1.69 MW.

## Solution of Problem 10.14

**Prob 10.15** A hydrogen production system using direct dissociation of water is to operate at 1500 K. To have adequate hydrogen flux through a palladium filter used to separate the gas from oxygen and water vapor, it is necessary to have a hydrogen pressure differential of 5 atmospheres across the membrane. Assume that the pure hydrogen side is at 1 atmosphere. What pressure must be used on the water vapor side? Repeat for  $T = 3000$  K.

.....  
If  $F$  is the fraction of the water that is dissociated, then the hydrogen pressure will be

$$p_{H_2} = \frac{F}{1 + F/2} p = p_{H_2},$$

where  $p$  is the pressure on the water vapor side.

$$p = p_{H_2} \frac{1 + F/2}{F}.$$

The equilibrium constant is

$$\begin{aligned} K &= \frac{F^{1/2}}{\sqrt{2}(1-F)(1+F/2)^{1/2}} p^{1/2} \\ &= \frac{F^{1/2}}{\sqrt{2}(1-F)(1+F/2)^{1/2}} * \left[ p_{H_2} \frac{1 + F/2}{F} \right]^{1/2} = \sqrt{\frac{p_{H_2}}{2}} \frac{F}{1-F}. \\ F &= \frac{1}{\sqrt{\frac{p_{H_2}}{2}} \frac{1}{K} + 1}. \end{aligned}$$

The value of the equilibrium constant at 1500 K is  $40.43 \times 10^{-6}$ , and the desired hydrogen pressure is 5 atmos, therefore,

$$F = \frac{1}{\sqrt{\frac{5}{2}} \frac{1}{40.43 \times 10^{-6}} + 1} = 25.6 \times 10^{-6}$$

$$p = 5 \frac{1 + 25.6 \times 10^{-6}/2}{25.6 \times 10^{-6}} = 195,600 \quad \text{atmos.}$$

The required pressure is 196,000 atmospheres.

This is such a large pressure to make essentially impossible to build the system.

## Solution of Problem 10.15

If we now raise the temperature to 3000 K—which corresponds to an equilibrium constant of  $45.9 \times 10^{-3}$ —, we will find

$$F = \frac{1}{\sqrt{\frac{5}{2} \frac{1}{45.9 \times 10^{-3}} + 1}} = 28.2 \times 10^{-3}$$

and

$$p = 5 \frac{1 + 28.2 \times 10^{-3}/2}{28.2 \times 10^{-3}} = 180 \quad \text{atmos.}$$

The required pressure is 180 atmospheres.

Now the total pressure is not impossibly large but the temperature is too high to permit a practical implementation.

---

## Solution of Problem 10.15



**Prob 10.16** An electrolyzer is made of a MEA that has a specific resistance,  $\Re = 65 \mu\Omega \text{ m}^2$ . Each cell is to produce 100 grams of hydrogen per hour. The current efficiency is 100%.

**a. What is the current through each cell?**

.....  
If each cell is to produce 100 grams (0.1 kg) of hydrogen per hour, it must produce  $27.78 \times 10^{-6} \text{ kg/s}$  or  $13.89 \times 10^{-6} \text{ kilomoles/s}$ . The needed current is

$$I = n_e N_0 q \dot{N} = 2 \times 6.022 \times 10^{26} \times 1.6 \times 10^{-19} \times 13.89 \times 10^{-6} = 2,677 \text{ A.} \quad (1)$$

The current through the cell is 2,677 A.

---

**b. The  $V$ - $I$  characteristic is**

$$V = V_{rev} + V_{offset} + RI,$$

where  $V_{offset}$  is a constant offset voltage of 0.1 V.

The price of electricity is \$0.05/kWh. The price of the electrolyzer is proportional to the active area of the cell and is \$10,000 per square meter of active area. The cost of money is 12% per year. The only costs to be considered are those of investment and of the electric energy.

Temperature of operation is 298 K.

The plant operates continuously throughout the year.

In assembling the electrolyzer, you can choose the active area of the cell. What current density results in the most economical hydrogen production?

.....  
At 298 K, the reversible voltage in a liquid water electrolyzer is 1.231 V. Hence, the  $V$ - $I$  characteristic is (in terms of  $\Re$ ),

$$V = V_{rev} + V_{offset} + \frac{\Re}{A} I, \quad (2)$$

where  $A$  is the active area of the cell.

$$V = 1.231 + 0.1 + \frac{65 \times 10^{-6}}{A} 2677 = 1.331 + \frac{0.174}{A} \quad (3)$$

Introducing the numerical values,

The electric input power to the electrolyzer is

$$P = VI = \left(1.331 + \frac{0.174}{A}\right) \times 2677 = 3563 + \frac{465.8}{A} \text{ W.} \quad (4)$$

The electric energy used in 1 hour is  $3.563 + 0.4658/A$  kWh, and the cost of electricity per hour is

**Solution of Problem 10.16**

$$C_e = (3.563 + 0.4658/A) \times 0.05 = 0.1782 + \frac{0.02329}{A} \quad \$/\text{h}. \quad (5)$$

The equipment cost \$10,000/m<sup>2</sup>. The annual cost of investment is  $0.12 \times 10,000 = 1,200$  \$/m<sup>2</sup>, and the hourly cost of investment is  $1,200/8760 = 0.137$  \$/m<sup>2</sup>. Thus,

$$C_{inv} = 0.137A \quad \$/\text{h}, \quad (6)$$

and the cost of the produced hydrogen is

$$C_H = 0.1782 + \frac{0.02329}{A} + 0.137A \quad \$/\text{h}. \quad (7)$$

$$\frac{dC_H}{dA} = -\frac{0.02329}{A^2} + 0.137 = 0. \quad (8)$$

$$A = 0.412 \quad \text{m}^2. \quad (9)$$

This corresponds to a current density of  $2677/0.412 = 6,490$  A/m<sup>2</sup>.

The most economical current density is 6,490 A/m<sup>2</sup>.

## Solution of Problem 10.16

**Prob 10.17** It is difficult to design containers that can operate at the extreme high temperature required to thermally dissociate water. Let us assume, optimistically, that temperatures of 2800 K can be handled. A 1-m<sup>3</sup> canister contains 100 g of liquid water when cold. It is, then, heated to 2800 K and part of the water will dissociate into hydrogen.

**a. How many grams of hydrogen are formed?**

.....  
The dissociation constant,  $K_p$  for the  $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$  reaction at 2800 K is

$$K_p = 847.3 \exp - \frac{246 \times 10^6}{RT} = 847.3 \exp - \frac{246 \times 10^6}{8314 \times 2800} = 21.8 \times 10^{-3}. \quad (1)$$

0.1 kg of water represent 0.00556 kmoles. At 2800 K and in a 1 m<sup>3</sup> volume, the vapor has a pressure of

$$p = \mu \frac{RT}{V} = 0.00556 \times \frac{8314 \times 2800}{1} = 129,300 \text{ Pa or } 1.276 \text{ atmos.} \quad (2)$$

This estimation of the gas pressure disregards the fact that some of the water has dissociated thus increasing the total number of moles in the gas. The real pressure is somewhat higher, but the error resulting from this assumption is small owing to the small amount of dissociation that occurs at 2800 K. As a matter of fact, in the present problem, the assumption causes an over-estimation of only 1.27% in the amount of free hydrogen.

Let us do the calculation more rigorously.

If a fraction,  $F$ , of the water dissociates at 2800 K, then the gas in the container will have a composition,

$$(1 - F) \text{H}_2\text{O} + F \text{H}_2 + \frac{1}{2}F \text{O}_2. \quad (3)$$

The number of kilomoles of gas in this mixture is

$$\mu = 0.00556(1 - F + F + \frac{1}{2}F) = 0.00556(1 + \frac{1}{2}F) \quad (4)$$

hence the gas pressure is  $p = 1.276(1 + \frac{1}{2}F)$ .

The fraction,  $F$ , of water dissociated is related to  $K_p$  by

$$\frac{F^{3/2}}{\sqrt{2 - 3F + F^3}} = \frac{K_p}{\sqrt{p}} = \frac{21.8 \times 10^{-3}}{\sqrt{1.276(1 + \frac{1}{2}F)}}. \quad (5)$$

A numerical solution yields  $F = 0.0855$  (it would have been 0.0866 under the simplifying assumption). Thus, the amount of dissociated water

## Solution of Problem 10.17

is  $0.0855 \times 100 = 8.55$  g. Since each 18 g of water corresponds to 2 g of hydrogen, the amount of free hydrogen is 0.95 g.

The amount of free hydrogen is 0.95 g.

This is a yield of 0.95%.

- b. The amount of free hydrogen is going to be small. What would happen if instead of 100 g of water, you had used 10 kg?**

.....  
In this case, the pressure of the vapor at 2800 K would be about 100 times that of Item 1. It would be around 127.6 atmos.

$$\frac{F^{3/2}}{\sqrt{2 - 3F + F^3}} = \frac{K}{\sqrt{p}} = \frac{21.8 \times 10^{-3}}{\sqrt{127.6}} = 0.00193. \quad (6)$$

Notice that we did not bother to calculate the pressure precisely because, under the much higher pressure in this part of the problem, a much smaller fraction of the water dissociates (Le Chatelier's law).

The solution to the equation above is  $F = 0.0194$ , and  $10,000 \times 0.0194 = 194$  g of water dissociate resulting in  $194/9 = 21.6$  g of hydrogen, a yield of 0.216%. Thus, increasing the amount of water decreased the yield.

21.6 g of hydrogen are produced.

## Solution of Problem    10.17

**Prob 10.18** Ammonia is perhaps the most important of fertilizers. It provides nitrogen essential to the growth of plants. In 2000, world-wide production of ammonia exceeded 120 million tons per year.

All ammonia is produced by the Harber-Bosch process based on the reaction:



Enthalpy of formation:  $\Delta \bar{h}_{f_{\text{NH}_3}}^\circ = -46.19 \text{ MJ/kmole}$ .

- a. Is the equilibrium toward the ammonia side favored by raising or by lowering the pressure in the reactor?**

.....  
Le Chatelier's Law.

There are 4 kilomoles of gases in the left hand side of the equation and only two kilomoles on the right hand side. Consequently, increasing the pressure, increases the ammonia concentration.

- b. Is the equilibrium toward the ammonia side favored by raising or by lowering the temperature of the gases?**

.....  
Still Le Chatelier's Law.

The heat of formation of ammonia is smaller than zero—heat is released by the reaction, i.e., the reaction is exothermic. Lowering the temperature in the reactor will favor the production of ammonia.

- c. Clearly, it is not possible to take the favorable conditions of pressure and temperature to an extreme. Give one good reason for limiting pressure and temperature extremes.**

.....  
10.19:1 The higher the pressure, the more expensive the equipment, especially the main gas compressor. The original Fritz Haber proposal was for 1000 atmospheres. Economic considerations have lower the pressure in modern plants to a little over 100 atmospheres.

Low temperatures favor ammonia in equilibrium, but the kinetics of the reaction become very unfavorable. Even with modern catalysts, fairly high temperatures are required to produce ammonia at an acceptable rate.

## Solution of Problem 10.18

**Prob 10.19** Nitric oxide, NO, is a gas of great importance in the biology of mammals where it plays a central role in the operation of cells. It is also a serious pollutant because it readily combines with oxygen to form the toxic gas, NO<sub>2</sub>.

The nitrogen in the air can react with the oxygen according to



This causes the formation the undesired NO which, reacting with atmospheric oxygen and water vapor, is converted to nitric acid and causes acid rain to fall. NO is also a source of photochemical smog and a destroyer of the ozone layer.

Here are some pertinent thermodynamic data:

Enthalpies of formation:

	298.15 K	6000 K	
NO	90.37	298.87	MJ/kmole

Entropies:

	298.15 K	6000 K	
N <sub>2</sub>	195.7	280.0	kJ K <sup>-1</sup> kmole <sup>-1</sup>
O <sub>2</sub>	205.0	313.3	kJ K <sup>-1</sup> kmole <sup>-1</sup>
NO	210.6	369.4	kJ K <sup>-1</sup> kmole <sup>-1</sup>

Equilibrium constant,  $K_p = 4.522 \exp -\frac{90.58 \times 10^6}{RT}$ .

- a. Does the reaction that generates NO from N<sub>2</sub> and O<sub>2</sub> proceed spontaneously at room temperature? If you say it does, then you have to explain how come there is so little NO in the air. If you say it does not, then how come there is a problem with NO pollution?

.....  
Nature has two tendencies:

- systems tend toward a state of lowest energy,
- systems tend to states of maximum entropy.

At STP, going from left to right, the reaction of Equation 1 is endothermic because the  $\Delta \bar{h}_{f_{NO}}^\circ$  is positive. In other words NO has more energy than the nitrogen plus oxygen from which it is formed. The reaction goes up-hill. From the point of view of the 1st Law of thermodynamics, the reaction should proceed from right to left.

Notice however that the entropy of the gases in the left hand side of the equation is  $\frac{1}{2}(195.7 + 205.0) = 200.4 \text{ kJ K}^{-1}\text{kmole}^{-1}$ , while on the right hand side has an entropy of  $210.6 \text{ kJ K}^{-1}\text{kmole}^{-1}$ . Thus, going from left to right, the reaction causes an increase in entropy of  $210.6 - 200.4 = 10.2 \text{ kJ K}^{-1}\text{kmole}^{-1}$ . Consequently, from the 2nd Law point of view, nitrogen wants to react with oxygen to produce nitric oxide. Which of the two effects (1st and 2nd Laws) dominates?

## Solution of Problem 10.19

The energy associated with the entropy change is  $T\Delta S = 298 \times 10,200 = 3.04 \text{ MJ/kmole}$ .

We have to compare the unfavorable energy balance of 90.4 MJ/kmole owing to the 1st Law with the favorable 3.04 MJ/kmole that comes from 2nd Law considerations. Clearly, in this case, the 1st Law beats the 2nd Law and the reaction favors the dissociation of NO, not its production.

Note that what we did was to take the difference  $\Delta H - T\Delta S$ . This is the free energy change owing to the reaction ( $\Delta G$ ). In other words, the reaction will proceed in the direction that causes  $\Delta G$  to be negative, i.e., the reaction proceeds in the direction that reduces the free energy of the system.

The problem is that, although at room temperature, the nitrogen and oxygen in the air do not react, they will do so at elevated temperatures like those created by lightning or inside the cylinders of IC engines.

**b. What happens when the gases are at 6000 K? If the reaction converts nitrogen and oxygen into nitric oxide, what fraction of the gas mixture, at equilibrium, consists of NO?**

At 6000 K, the free energy change owing to the reaction is

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S = 298.9 - 6000 \times [0.3694 - \frac{1}{2}(0.2800 + 0.3133)] \\ &= -13.85 \quad \text{MJ/kmole}\end{aligned}\quad (2)$$

Since the  $\Delta G$  is negative, there is a drive to dissociate nitric oxide into its constituents,  $\text{N}_2$  and  $\text{O}_2$ .

The equilibrium constant at 6000 K is,

$$K_p = 4.522 \exp - \frac{90.58 \times 10^6}{6000 \times 8314} = 0.7358. \quad (3)$$

When a fraction,  $F$ , of nitrogen is transformed into NO, the resulting mixture has the composition,

$$\frac{1}{2}(1-F)\text{N}_2 + \frac{1}{2}(1-F)\text{O}_2 + F \text{ NO}. \quad (4)$$

The total number of kilomoles is,

$$\frac{1-F}{2} + \frac{1-F}{2} + F = 1. \quad (5)$$

The partial pressures are,

$$p_{\text{N}_2} = \frac{1-F}{2}, \quad (6)$$

## Solution of Problem 10.19

$$p_{O_2} = \frac{1-F}{2}, \quad (7)$$

$$p_{NO} = F, \quad (8)$$

The equilibrium constant is

$$K_p = \frac{p_{NO}}{\sqrt{p_{N_2}}\sqrt{p_{O_2}}} = \frac{2F}{1-F} \quad (9)$$

$$F = \frac{K_p}{2 + K_p} = \frac{0.7358}{2 + 0.7358} = 0.269 \quad (10)$$

At 6000 K and 1 atmos, 26.9% of the gas is NO.

- 
- c. You will have found from Item 2 that at 6000 K (easily reached during a lightning stroke) substantial amounts of NO are produced. But the air quickly cools down and as we saw from Item 1, at low temperature the equilibrium is toward complete dissociation of NO. So, how come NO lingers around constituting a serious pollutant?

.....

True, given enough time all the NO will decay into nitrogen and oxygen. However, the reaction is exceedingly slow. That is why the exhaust gases of an IC engine have to be passed over a catalysts to accelerate the decay of NO.

---

## Solution of Problem 10.19



**Prob 10.20** Ammonia,  $\text{NH}_3$ , is produced by direct combination of nitrogen extracted from air with hydrogen obtained from fossil fuels, from water or from both. A large industrial ammonia plant can produce more than 1000 tons of the substance, per day.

In some countries, it may be better to have a distributed ammonia production system to avoid the difficulties of transporting this substance over long distances. Assume we want to produce only 3 tons of ammonia in each of a number of small plants using electrolytic hydrogen. The plants will work continuously, 24 hours per day.

**a - How many kilograms of hydrogen will have to be produced each day?**

.....  
The ammonia reaction is



This means that 1 kilomole of ammonia (molecular mass, 17 daltons), requires 3 kmols of H (molecular mass 1 dalton). Thus, by mass, the ratio of hydrogen to ammonia is 3:17.

3000 kg of ammonia require  $3000 \times 3/17 = 529.4$  kg of  $\text{H}_2$ .

529 kg of hydrogen must be produced per day.

The above is a rate of 22 kg/h or 0.0061 kg/s or 0.0031 kmols per second.

---

**b - Consider an electrolyzer cell represented by a simple voltage source,  $V_0 = 1.35$  V, in series with an internal resistance,  $R_{int} = 0.0005 \Omega$ . Operating conditions are at RTP.**

**When operating at 80% efficiency, how many cells (connected in series) have to be used to produce hydrogen at the rate required by Item a?**

.....  
We note that the reversible voltage of a water electrolyzer at RTP is 1.231 V. A  $V_0 = 1.35$  V, suggests that the cell has losses other than those owing to series resistance. The efficiency of an electrolyzer is

$$\eta = \frac{1.484}{V} = 0.80, \quad (2)$$

from which,

$$V = \frac{1.484}{0.8} = 1.855 \text{ V}. \quad (3)$$

**Solution of Problem 10.20**

From the given characteristics of the cell,

$$V = 1.885 = V_0 + R_{int}I = 1.35 + 0.0005I \quad (4)$$

Solving for I, we get = 1,010 A.

This current will produce

$$\dot{N} = \frac{I}{2qN_0} = \frac{1,010}{2 \times 1.6 \times 10^{-19} \times 6.021 \times 10^{26}} = 5.24 \times 10^{-6} \text{ kmole (H}_2\text{)/s.} \quad (5)$$

The total number of cells needed is

$$N = \frac{0.0031}{5.24 \times 10^{-6}} \approx 592 \text{ cells.} \quad (6)$$

592 cells are needed.

**c - How much heat must each cell reject when operating under the conditions of Item b?**

.....  
The heat rejected by each cell is

$$\dot{Q} = (V - 1.484)I = (1.855 - 1.484) \times 1010 = 374.7 \text{ W.} \quad (7)$$

Heat rejected per cell is 374.7 W.

**d - If the current driving the electrolyzer is reduced sufficiently, the device will act as a heat pump. Calculate what current maximizes the amount of heat drawn in by each cell. Calculate the amount of heat drawn in under such conditions.**

.....  
The heat the cell exchanges with the environment is

$$\dot{Q} = (1.35 + 0.0005I - 1.484)I. \quad (8)$$

$$\frac{d\dot{Q}}{dI} = -0.134 + 2 \times 0.0005I = 0, \quad (9)$$

hence, the current that maximizes cooling is

$$I = \frac{0.134}{0.001} = 134 \text{ A.} \quad (10)$$

and the heat pumped in is (from Equation 8),

$$\dot{Q} = 8.98 \text{ W.} \quad (11)$$

The current that maximizes cooling is 134 A.  
At this point, the each electrolyzer cell absorbs almost 9 W of heat.

## Solution of Problem 10.20

**Prob 10.21**    An ideal solid polymer electrolyzer operating at 60 C, produces H<sub>2</sub> and O<sub>2</sub> at 1 atmosphere pressure. It draws a current of 300 A and produces hydrogen at a rate of  $1.557 \times 10^{-6}$  kmoles/sec. What is the production rate (still using 300 A) if the operating temperature is raised to 90 C and all pressures are doubled?

.....  
The production rate depends only on the current, not on temperature or pressure of the products. Hence, the production rate is not altered by the indicated change in operation conditions.

The production rate is still $1.557 \times 10^{-6}$ kmoles/s.
---

---

Solution of Problem    10.21

**Prob 10.22** What is the partial pressure of  $O_2$  when 9 g of pure water are heated to 3000 K in a 100 liter container?

.....  
The value of the (pressure) equilibrium constant for water is given by

$$K_p = 847.3 \exp - \frac{246 \times 10^6}{RT}. \quad (1)$$

When  $T = 3000$ ,  $K_p = 0.0441$ .

The amount of water in the container is  $\mu_0 = 0.0005$  kmoles.

When a fraction,  $F$ , of the water dissociates, the composition of the gas is  $(1 - F) H_2O + F H_2 + \frac{1}{2} F O_2$ .

This gas contains  $\mu_0(1 - F + F + \frac{1}{2}F) = \mu_0(1 + \frac{1}{2}F)$  kilomoles.

$$\mu = \mu_0(1 + \frac{1}{2}F), \quad (2)$$

The water–hydrogen–oxygen mixture, at 3000 K will be at a pressure

$$\begin{aligned} p &= \mu_0(1 + \frac{1}{2}F) \frac{RT}{V} = 0.0005(1 + \frac{1}{2}F) \times \frac{8314 \times 3000}{0.1} \\ &= 12.47 \times 10^3(1 + \frac{1}{2}F) \text{ Pa} \quad \text{or} \quad 1.23(1 + \frac{1}{2}F) \text{ atmos.} \end{aligned} \quad (3)$$

The fraction,  $F$ , of water dissociated is related to  $K_p$  by

$$\frac{F^{3/2}}{\sqrt{2 - 3F + F^3}} = \frac{K_p}{\sqrt{p}} = \frac{0.0441}{\sqrt{1.23(1 + \frac{1}{2}F)}}. \quad (4)$$

A numerical solution leads to  $F = 0.133$ . This means that the total pressure of gas is

$$p = 1.23(1 + \frac{1}{2}F) = 1.23 \times \left(1 + \frac{0.133}{2}\right) = 1.31 \text{ atmos.} \quad (5)$$

Of this, a fraction,  $F/2 = 0.0665$ , is the partial pressure of oxygen,

$$p_{O_2} = 0.0665 \times 1.23(1 + \frac{1}{2}0.133) = 0.087 \text{ atmos.} \quad (6)$$

The partial pressure of oxygen is 0.087 atmospheres.

## Solution of Problem 10.22

**Prob 10.23**    The current through a 2-cell electrolyzer is 200 A. The total voltage is 4 V. What is the hydrogen production rate? What is the heat power generated?

.....

$$\dot{N} = 2 \frac{I}{n_e q N_0} = 2 \frac{200}{2 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{26}} = 2.08 \times 10^{-6} \text{ kmol/s.} \quad (1)$$

Hydrogen production rate is  $2.08 \times 10^{-6}$  kilomoles per second.

$$\dot{Q} = (V - 1.484)I = (4 - 2 \times 1.484) \times 200 = 206 \text{ W.} \quad (2)$$

Heat is generated at the rate of 206 W.

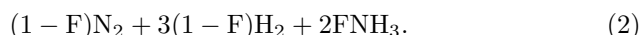
Solution of Problem    10.23

**Prob 10.24 The ammonia synthesis reaction is**

A stoichiometrically correct mixture of reactants is fed to a reactor vessel and is kept at a total pressure of 1 atmosphere and at a temperature,  $T$ . After a sufficient time has elapsed equilibrium between the reactants and the product, ammonia, has been established. It is found that the gas pressure of the  $\text{NH}_3$  in the reactor is 0.02053 atmospheres.

**a – Determine the equilibrium constant,  $K_p$ , of the reaction at the temperature  $T$ . What is wanted is a simple numerical answer such as “ $K_p = x.xxx$ .”**

.....  
If a fraction,  $F$ , of the initial hydrogen is used up in the reaction, then  $(1 - F)\text{N}_2$  is left over and an amount,  $F\text{N}_2$ , is used in forming  $2F\text{NH}_3$  kilomoles of ammonia. This uses up  $6F$  kilomoles of H. Since we started up with 3 kilomoles of  $\text{H}_2$ , i.e., 6 kilomoles of H, we have now left  $6(1 - F)$  kilomoles of H or  $3(1 - F)$  of  $\text{H}_2$ . The mixture has the composition below:



This mixture has a total number of kilomoles of

$$N_{TOTAL} = (1 - F) + 3(1 - F) + 2F = 2(2 - F). \quad (3)$$

The corresponding partial pressures are

$$p_{\text{N}_2} = \frac{1}{2} \frac{1 - F}{(2 - F)} \quad (4)$$

$$p_{\text{H}_2} = \frac{3}{2} \frac{(1 - F)}{(2 - F)} \quad (5)$$

$$p_{\text{NH}_3} = \frac{F}{(2 - F)} \quad (6)$$

The equilibrium constant is

$$K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3} = \frac{\left(\frac{F}{(2-F)}\right)^2}{\left(\frac{1}{2} \frac{1-F}{(2-F)}\right) \left(\frac{3}{2} \frac{(1-F)}{(2-F)}\right)^3} = 0.5926 \frac{(2-F)^2 F^2}{(1-F)^4} \quad (7)$$

The partial pressure of ammonia was given as 0.02053 atmospheres. Remember that the total pressure is kept at 1 atmosphere. Since the partial pressure of ammonia is  $F/(2 - F)$  (see Equation 6), we have,

$$\frac{F}{2 - F} = 0.02053. \quad (8)$$

from which,  $F = 0.04023$ .

## Solution of Problem 10.24

The corresponding pressure of nitrogen is (from Equation 4)

$$p_{\text{N}_2} = \frac{1}{2} \times \frac{1 - 0.04023}{2 - 0.04023} = 0.2449 \quad (9)$$

and that of hydrogen is 3 times larger:

$$p_{\text{H}_2} = 3 \times 0.24945 = 0.7346. \quad (10)$$

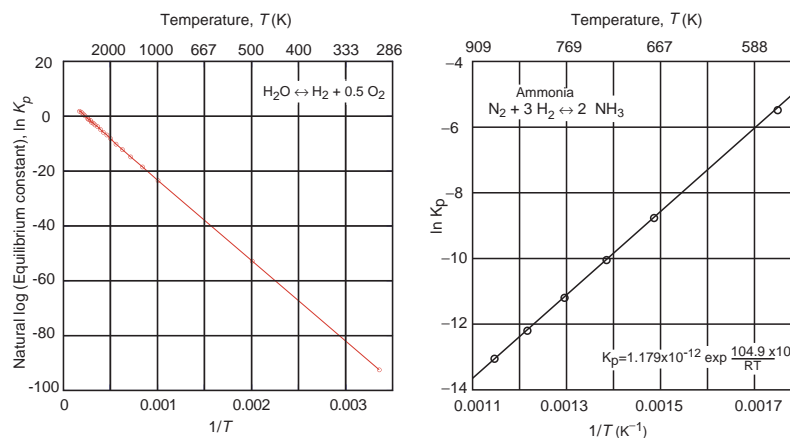
Check:  $0.02053 + 0.2449 + 0.7346 = 1.0000$ .

Introducing the value of  $F$  into Equation 7, The equilibrium constant,  $K_p$ , becomes,

$$K_p = \frac{0.02053^2}{0.2449 \times 0.7346^3} = 0.00434. \quad (11)$$

$$K_p = 0.00434.$$

It is worth observing that, since the reaction is exothermic (you can think of hydrogen burning in an atmosphere of nitrogen), according to Le Chatelier's law, the *higher* the temperature, the *smaller* the equilibrium constant. The slope of the  $\ln(K_p)$  versus  $1/T$  graph is the opposite of the one in Figure 10.11 of the Text which is for an endothermic reaction.



**Figure 10.1** Natural logarithm of the equilibrium constant for the dissociation of water (left) and synthesis of ammonia (right) versus inverse temperature. Water dissociation is endothermic (negative slope) while ammonia synthesis is exothermic (positive slope).

**b – What is the partial pressure of the ammonia in the mixture if the overall pressure is raised to 200 atmospheres? The temperature is still the same as in Part a of this problem.**

.....

**Solution of Problem 10.24**

Generalizing Equation 7 so that it applies to arbitrary pressures leads to

$$K_p = 0.5926 \frac{(2-F)^2 F^2}{(1-F)^4} p^{-2} \quad (12)$$

where  $p$  is in atmospheres. To get the pressure dependence, we just multiplied each of the partial pressures (Equations 4, 5, 6, ) by  $p$ .

The equilibrium constant, although temperature dependent, does not change with pressure, hence, since we are still at temperature,  $T$ , of Part a,  $K_p$  is still equal to 0.00434, and, Equation 12 becomes,

$$0.00434 = 0.5926 \frac{(2-F)^2 F^2}{(1-F)^4} 200^{-2} \quad (13)$$

$$293.0 = \frac{(2-F)^2 F^2}{(1-F)^4} \quad (14)$$

The solution is  $F = 0.765$  which leads to an ammonia pressure of

$$p_{NH_3} = 200 \frac{0.765}{2 - 0.765} = 123.9 \text{ atmos.} \quad (15)$$

The ammonia pressure is 124 atmospheres  
(62% of the total 200 atmospheres pressure).

## Solution of Problem 10.24



**Prob 10.25** An electrolyzer cell requires 1.6 V to drive 10 mA through it and 2 V to drive 1000 A through it.

If you use 100 such cells in series, how much power is required to produce 100 kg of hydrogen per day?

.....  
The typical  $V$ - $I$  characteristic of an electrolyzer is

$$V = V_{oc} + R_{int}I, \quad (1)$$

Since 10 mA is essentially zero compared with 1000 A, we can take the open-circuit voltage as 1.6 V. We then have

$$V = 1.6 + R_{int}I \quad (2)$$

Using the voltage of 2 V and the corresponding current of 1000 A, we find that  $R_{int} = 0.0004$  ohms. Thus

$$V = 1.6 + 0.0004I, \quad (3)$$

To produce 100 kg of hydrogen per day, each of the 100 cells must produce 1 kg/ day.

$$1 \text{ kg/day} = 0.5 \text{ kmole/day} = 579 \times 10^{-8} \text{ kmole/sec.}$$

$$I = 2qN_0\dot{N} = 192.7 \times 10^6 \dot{N} = 1116 \text{ A} \quad (4)$$

The power used by each electrolyzer is

$$P_{in} = (1.6 + 0.0004 \times 1116) \times 1116 = 2284 \text{ W.} \quad (5)$$

The 100-electrolyzer battery uses 228,400 W.

---

**Repeat for a 200-cell electrolyzer battery.**

.....  
With 200 cells, each has to produce only  $290 \times 10^{-8}$  kmole/sec. This requires a current of 558 A and a power consumption of

$$P_{in} = (1.6 + 0.0004 \times 558) \times 558 = 1017 \text{ W per unit.} \quad (6)$$

200 cells use 203,470 W.

---

**Which of the two configurations produces the cheaper hydrogen?**

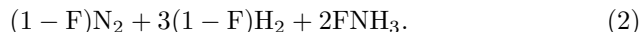
.....  
The 100-cell battery uses 228.4 kW of energy, whereas the 200-cell one uses only 203.5 kW. It can be seen that the larger number of cells leads to somewhat greater efficiency, but, probably, to more expensive hydrogen because of the much larger capital cost of the equipment.

## Solution of Problem 10.25

**Prob 10.26 The ammonia synthesis reaction is**

A stoichiometrically correct mixture of reactants is fed to a reactor vessel and is kept at a total pressure of 1 atmosphere and at a temperature,  $T$ . After a sufficient time has elapsed equilibrium between the reactants and the product, ammonia, has been established. It is found that the gas pressure of the  $\text{NH}_3$  in the reactor is 0.02053 atmospheres. Determine the equilibrium constant,  $K_p$ , of the reaction at the temperature  $T$ . What is wanted is a simple numerical answer such as " $K_p = x.xxx$ ."

.....  
If a fraction,  $F$ , of the initial hydrogen is used up in the reaction, then  $(1 - F)\text{N}_2$  is left over and an amount,  $F\text{N}_2$ , is used in forming  $2F\text{NH}_3$  kilomoles of ammonia. This uses up  $6F$  kilomoles of H. Since we started up with 3 kilomoles of  $\text{H}_2$ , i.e., 6 kilomoles of H, we have now left  $6(1 - F)$  kilomoles of H or  $3(1 - F)$  of  $\text{H}_2$ . The mixture has the composition below:



As a check, consider that what was introduced into the reactor were 2 kilomoles of N and 6 of H. Clearly after the reaction reaches equilibrium, the number of atoms of each element cannot have changed. In fact we have  $2(1 - F)$  kmols of free nitrogen plus  $2F$  kilomoles of nitrogen in the ammonia. This adds up to 2 exactly 2 kilomoles of nitrogen atoms as before the reaction. The Fs must cancel out. You can do the same for the H.

This mixture has a total number of kilomoles of

$$N_{TOTAL} = (1 - F) + 3(1 - F) + 2F = 2(2 - F). \quad (3)$$

The corresponding partial pressures are

$$p_{\text{N}_2} = \frac{1}{2} \frac{1 - F}{(2 - F)} \quad (4)$$

$$p_{\text{H}_2} = \frac{3}{2} \frac{(1 - F)}{(2 - F)} \quad (5)$$

$$p_{\text{NH}_3} = \frac{F}{(2 - F)} \quad (6)$$

The equilibrium constant is

$$K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3} = \frac{\left(\frac{F}{(2 - F)}\right)^2}{\left(\frac{1}{2} \frac{1 - F}{(2 - F)}\right) \left(\frac{3}{2} \frac{(1 - F)}{(2 - F)}\right)^3} = 0.5926 \frac{(2 - F)^2 F^2}{(1 - F)^4} \quad (7)$$

**Solution of Problem 10.26**

The partial pressure of ammonia was given as 0.02053 atmospheres. Remember that the total pressure is kept at 1 atmosphere. Since the partial pressure of ammonia is  $F/(2 - F)$  (see Equation 6), we have,

$$\frac{F}{2 - F} = 0.02053. \quad (8)$$

from which,  $F = 0.04023$ .

The corresponding pressure of nitrogen is (from Equation 4)

$$p_{\text{N}_2} = \frac{1}{2} \times \frac{1 - 0.04023}{2 - 0.04023} = 0.2449 \quad (9)$$

and that of hydrogen is 3 times larger:

$$p_{\text{H}_2} = 3 \times 0.2449 = 0.7346. \quad (10)$$

Check:  $0.02053 + 0.2449 + 0.7346 = 1.0000$ .

Introducing the value of  $F$  into Equation 7, The equilibrium constant,  $K_p$ , becomes,

$$K_p = \frac{0.02053^2}{0.2449 \times 0.7346^3} = 0.00434. \quad (11)$$

$K_p = 0.00434.$

Note that if you write the reaction as



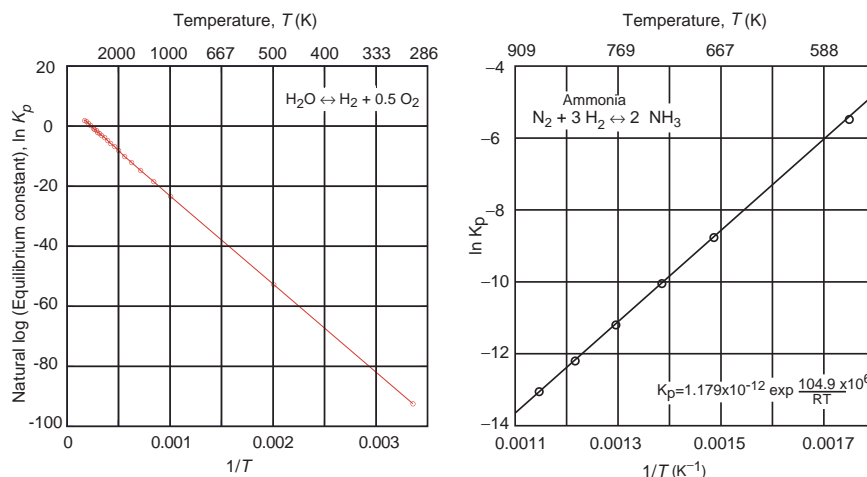
you get a completely different value of  $K_p$ :

$$K_p = \frac{0.02053}{0.2449^{1/2} \times 0.7346^{3/2}} = 0.0659. \quad (13)$$

$K_p = 0.0659.$

It is worth observing that, since the reaction is exothermic (you can think of hydrogen burning in an atmosphere of nitrogen), according to Le Chatelier's law, the *higher* the temperature, the *smaller* the equilibrium constant. The slope of the  $\ln(K_p)$  versus  $1/T$  graph is the opposite of the one in Figure 10.11 of the Text which is for an endothermic reaction.

## Solution of Problem 10.26



**Figure 10.2** Natural logarithm of the equilibrium constant for the dissociation of water (left) and synthesis of ammonia (right) versus inverse temperature. Water dissociation is endothermic (negative slope) while ammonia synthesis is exothermic (positive slope).

**b – What is the partial pressure of the ammonia in the mixture if the overall pressure is raised to 200 atmospheres? The temperature is still the same as in Part a of this problem.**

.....  
 Generalizing Equation 9 to include arbitrary pressures leads to

$$K_p = 0.5926 \frac{(2 - F)^2 F^2}{(1 - F)^4} p^{-2} \quad (14)$$

where  $p$  is in atmospheres. To get the pressure dependence, we just multiplied each of the partial pressures (Equations 6, 7, 8, ) by  $p$ .

The equilibrium constant, although temperature dependent, does not change with pressure, hence, since we are still at temperature,  $T$ , of Part a,  $K_p$  is still equal to 0.00434, and, Equation 14 becomes,

$$0.00434 = 0.5926 \frac{(2 - F)^2 F^2}{(1 - F)^4} 200^{-2} \quad (15)$$

$$293.0 = \frac{(2 - F)^2 F^2}{(1 - F)^4} \quad (16)$$

The solution is  $F = 0.765$  which leads to an ammonia pressure of

$$p_{\text{NH}_3} = 200 \frac{0.765}{2 - 0.765} = 123.9 \text{ atmos.} \quad (17)$$

## Solution of Problem 10.26

The ammonia pressure is 124 atmospheres  
(62% of the total 200 atmospheres pressure).

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Solution of Problem 10.26

**Prob 10.27** Consider an electrolyzer and its power supply which can be modeled as a constant voltage source,  $V_S = 2.50$  V, in series with an internal resistance,  $R_S = 457 \mu\Omega$ . The electrolyzer, at RTP, can be modeled as an ideal device ( $V_{rev} = 1.231$  V) in series with a internal resistance,  $R_{int} = 723 \mu\Omega$ .

What is the hydrogen production rate at RTP?

What is the production rate if the product gases are delivered at 500 atmospheres, but the operating temperature is still 298.1 K?

Calculate, for both cases, the amount of heat the electrolyzer must exchange with the environment.

Assume that the electrolyzer performance is not degraded by the higher gas pressure. Quote the gas production in mg/s.

Disregard the energy necessary to force water into the high pressure electrolyzer.

.....  
At RTP:

The current through the electrolyzer is

$$I = \frac{2.50 - 1.231}{(457 + 723) \times 10^{-6}} = 1075 \quad \text{A.}$$

Thus the hydrogen production rate is

$$\begin{aligned} \dot{N}_{H_2} &= \frac{I}{2qN_0} \\ &= \frac{1077}{2 \times 1.60 \times 10^{-19} \times 6.02 \times 10^{23}} = 5.58 \times 10^{-6} \quad \text{kmole (H}_2\text{)/s.} \end{aligned}$$

This corresponds to 11.2 mg/s.

The hydrogen production rate is 11.2 mg/s.

The voltage applied to the electrolyzer is

$$V = 1.231 + 723 \times 10^{-6} \times 1077 = 2.008 \quad \text{V.}$$

The amount of heat rejected by the electrolyzer is

$$W_{heat} = (2.008 - 1.482) \times 1075 = 565.4 \quad \text{W.}$$

Another way to calculate the shedded heat is to realize that the losses caused by the internal resistance are

$$W_{losses} = 1075^2 \times 723 \times 10^{-6} = 835.5 \quad \text{W.}$$

## Solution of Problem 10.27

From theses, a total of

$$W_{thermo} = \dot{N} \times T\Delta S \quad \text{W}$$

are absorbed by the electrolyzer because it is an endothermic device.

$$T\Delta S = \Delta H - \Delta G = 285.9 - 237.2 = 48.7 \quad \text{MJ/kmole.}$$

Hence,

$$W_{thermo} = 5.58 \times 10^{-6} \times 48.7 \times 10^6 = 271.8 \quad \text{W.}$$

The heat rejected is

$$W_{heat} = 835.5 - 271.8 = 563.7$$

This is about the same as the previously calculated value. The small different is due to round-off errors.

The electrolyzer must reject 565 W of heat.

At  $T = 298$  K and  $p = 500$  atmospheres:

Additional electric energy must be supplied to accomplish the isothermal gas compression. The amount of energy for this compression is

$$\begin{aligned} W_{compr.} &= RT \ln(500) + \frac{1}{2} RT \ln(500) = 8314 \times 298 \ln(500)^{1.5} \\ &= 23.1 \times 10^6 \quad \text{J/kmole.} \end{aligned}$$

This corresponds to an added voltage of

$$V_{compr.} = \frac{23.1 \times 10^6}{2 \times 1.60 \times 10^{-19} \times 6.02 \times 10^{26}} = 0.120 \quad \text{V.}$$

The current through the electrolyzer is now

$$I = \frac{2.50 - 1.231 - 0.12}{(457 + 723) \times 10^{-6}} = 974 \quad \text{A.}$$

Thus the hydrogen production rate is

$$\begin{aligned} \dot{N}_{H_2} &= \frac{I}{2qN_0} \\ &= \frac{974}{2 \times 1.60 \times 10^{-19} \times 6.02 \times 10^{26}} = 5.05 \times 10^{-6} \quad \text{kmole (H}_2\text{)/s.} \end{aligned}$$

## Solution of Problem 10.27

This corresponds to 10.1 mg/s.

The hydrogen production rate is 10.1 mg/s.

Compressing the gas does not alter the enthalpy change of the reaction—it is still 285.9 MJ/kmole and the “enthalpy voltage” is still 1.48 V.

To be sure,  $\Delta H = \Delta G + T\Delta S$  and  $\Delta G$  increased by  $RT \ln 500^{1.5}$ . However, owing to the isothermal compression the entropy changes by  $R \ln 500^{1.5}$  and, thus, the increase in  $\Delta G$  is exactly compensated by the decrease in  $T\Delta S$ .

The voltage applied to the electrolyzer is

$$V = 1.231 + 0.120 + 723 \times 10^{-6} \times 974 = 2.055 \quad \text{V.}$$

The amount of heat rejected by the electrolyzer is

$$W_{heat} = (2.055 - 1.482) \times 974 = 556 \quad \text{W.}$$

The electrolyzer must reject 558 W of heat.

## Solution of Problem 10.27