Question 1 – (Prob. 11.28) (30 pts., total) A solid canister (totally adiabatic and having no significant heat capacity), in a lab at Stanford University, has an internal volume of 10 liters and contains 3 kg of activated FeTiH$_{0.9}$ alloy at 300 K.

Assume that the heat capacity of H$_2$ is 30 kJ K$^{-1}$ kmole$^{-1}$, independently of temperature.

The alloy has the following characteristics:
- Density: 6200 kg m$^{-3}$.
- Atomic mass of iron: 55.8 daltons.
- Atomic mass of titanium: 47.9 daltons.
- Enthalpy change during absorption: -28.0 MJ kmole$^{-1}$.
- Entropy change during absorption: -106.1 kJ K$^{-1}$ kmole$^{-1}$.
- Heat capacity: 540 J K$^{-1}$ kg$^{-1}$.

Here is what happens:

The canister contains a certain amount of alloy nearly saturated with hydrogen and in addition there is some hydrogen in the dead space. The system is in equilibrium—the pressure of the gas in the dead space is equal to the plateau pressure of the alloy. Given the general conditions of the problem, the pressure in the dead space is 470 kPa (Question a) and the total amount of hydrogen in the system is 0.0148 kmoles of H$_2$ (Question b).

When a leak develops in the canister, hydrogen flows out and this flow stops when the pressure in the dead space is equal to the outside air pressure. Since the canister is in a lab at Stanford, the outside pressure is, almost certainly, 1 atmosphere. As the dead space gas escapes, the pressure decreases and some of the gas absorbed by the alloy will be desorbed in a tendency to re-establish the plateau pressure-dead space pressure equilibrium. The desorption, being endothermic, requires some heat input—the alloy and the dead space gas will, thus, cool down. Equilibrium is reached when the plateau pressure equals the dead space pressure which equals the outside environmental pressure which is 1 atmosphere. The problem is solved by seeking the temperature at which the plateau pressure is 1 atmosphere (Question 3).

a - (5 pts.) What is the pressure of the hydrogen gas in the dead space?

Clearly the alloy is in the plateau region and, thus, the gas pressure in
the dead space is equal to this plateau pressure:

\[ p = \exp \left( -\frac{\Delta S}{R} + \frac{\Delta H}{RT} \right) = \exp \left( \frac{106,100}{8314} - \frac{28 \times 10^6}{8314 \times 300} \right) = 4.64 \text{ atmos.} \]  

\( \text{Gas pressure is 4.64 atmospheres, or 470 kPa.} \)  

b - (5 pts.) What is the total amount of hydrogen in the canister?

The volume of the alloy (when depleted) is

\[ V_{\text{alloy}} = \frac{\text{mass}}{\text{density}} = \frac{3}{6200} = 0.00048 \text{ m}^3. \]  

The volume of the dead space is,

\[ V_{\text{dead space}} = 0.01 - 0.00048 = 0.00952 \text{ m}^3. \]  

\[ \mu_{\text{dead space}} = \frac{pV_{\text{dead space}}}{RT} = \frac{470,000 \times 0.00952}{8314 \times 300} = 0.0018 \text{ kmoles.} \]  

The formula mass of FeTi is 55.8+47.9=103.7 daltons (kg per k mole). Thus, 3 kg of alloy correspond to 0.0289 kmoles. The monoatomic hydrogen, H, is present in the proportion of 0.9 kmole per kmole of alloy, hence, the amount of hydrogen absorbed by the alloy is,

\[ \mu_H = 0.9 \times 0.0289 = 0.0260 \text{ kmoles of H or 0.013 kmoles of } H_2. \]  

The total amount of H\(_2\) in the canister is 0.0018+0.013=0.0148 kilomoles.

\[ \text{The canister contains 0.0148 kmoles of } H_2. \]  

3 - (20 pts.) If a leak develops and enough hydrogen escapes from the canister so that the flow of gas stops, how much gas is lost? Disregard diffusion of hydrogen driven by its concentration gradient.

As the hydrogen escapes from the canister, some of it will be desorbed from the alloy cooling both the alloy and the gas in the dead space. This causes the plateau pressure to fall. Note that the canister itself has negligible
heat capacity and is adiabatic. The flow will stop when the plateau pressure equal the external pressure of 1 atmosphere.

The alloy will be at the plateau pressure of 1 atmosphere when,

\[ T = \frac{\Delta H}{\Delta S} = \frac{28 \times 10^6}{106.1 \times 10^3} = 264 \text{ K.} \]  

This means that the system has to undergo a temperature change of,

\[ \Delta T = 300 - 264 = 36 \text{ K.} \]  

If one were to consider only the heat that has to be removed from the alloy, i.e., disregarding for the moment, the heat capacity of the hydrogen in the dead space, then the heat capacity of the system is simply the heat capacity, \( c_{alloy} \), of 3 kg of alloy which is \( 3 \times 540 = 1,620 \text{ J/K} \). The total amount of heat that has to be removed is

\[ \Delta H = 1,620 \times 36 = 58,300 \text{ J.} \]  

Each kmole of H\(_2\) desorbed requires \( 28 \times 10^6 \text{ MJ} \), hence, to remove 58,300 J, one needs to desorb \( 58,300/28 \times 10^6 = 0.0021 \) kmoles of H\(_2\).

Taking into account how much of the heat needed for desorption actually comes from the dead space gas, not from the alloy, is a bit tricky because we have no way to determine the varying temperature of the escaping hydrogen. Our best hope is to show that this heat contribution is not significant. Of course, one can simply assume that that is so, and I will accept such assumption. Let us make some very rough estimates. We note that prior to the onset of the leak, we had 0.0018 kmoles of H\(_2\) in the dead space. When the leak-induced flow ceases, the amount of gas in the dead space is,

\[ \mu_{ds,final} = \frac{pV}{RT} = \frac{10^5 \times 0.00952}{8314 \times 264} = 0.00043 \text{ kmoleH}_2, \]  

which means that, on average, something like 0.001 kmoles of gas contributed energy to the desorption. Using a \( \Delta T = 36 \text{ K} \), this amounts to

\[ 30,000 \times 0.001 \times 36 \approx 1,000 \text{ J.} \]  

This is negligible compared with the energy necessary to cool the alloy. Hence we can say that not much more than 0.0021 kmoles of H\(_2\) was desorbed.

Thus, the hydrogen losses amount to \( 0.0021/0.148=0.14 \) of the initial amount stored.

| Surprisingly, only 14% of the gas is lost. |

Question 2 – (Prob. 9.44) (70 pts) A single-cell hydrogen/oxygen fuel cell operating at 298.15 K has each reactant and the exhaust
water vapor at a pressure of 1 atmosphere. The cell has no transport losses.

Careful measurements have established the relationship below between the load current, \( I_L \), and the efficiency, \( \eta \):

\[
\begin{array}{c|c}
I_L & \eta \\
\hline
3 & 0.7735 \\
10 & 0.7146 \\
30 & 0.6388 \\
100 & 0.4791 \\
\end{array}
\]

Calculate the maximum power, \( P_{L_{\text{max}}} \), the cell can deliver to a load.

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Using

\[
P_{\text{in}} = \frac{\Delta h}{2qN_0} I_L = 1.2532 I_L, \quad (1)
\]

\[
P_L = \eta P_{\text{in}}, \quad (2)
\]

\[
P_H = P_{\text{in}} - P_L = 1.2532 (1 - \eta) I_L, \quad (3)
\]

\[
V_L = \frac{P_L}{I_L}, \quad (4)
\]

and

\[
\dot{N} = \frac{I_L}{2qN_0} = \frac{I_L}{192.9 \times 10^6}, \quad (5)
\]

we complete the above table:

<table>
<thead>
<tr>
<th>( I_L ) (A)</th>
<th>( \eta )</th>
<th>( P_{\text{in}} ) (W)</th>
<th>( P_L ) (W)</th>
<th>( P_H ) (W)</th>
<th>( V_L ) (V)</th>
<th>( \dot{N} ) ( \text{kmoles/s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.7735</td>
<td>3.7596</td>
<td>2.9080</td>
<td>0.8515</td>
<td>0.9693</td>
<td>( 1.5548 \times 10^{-8} )</td>
</tr>
<tr>
<td>10</td>
<td>0.7146</td>
<td>12.5321</td>
<td>8.9554</td>
<td>3.5767</td>
<td>0.8955</td>
<td>( 5.1828 \times 10^{-8} )</td>
</tr>
<tr>
<td>30</td>
<td>0.6388</td>
<td>37.5962</td>
<td>24.0164</td>
<td>13.5798</td>
<td>0.8005</td>
<td>( 1.5548 \times 10^{-7} )</td>
</tr>
<tr>
<td>100</td>
<td>0.4791</td>
<td>125.3208</td>
<td>60.0412</td>
<td>65.2796</td>
<td>0.6004</td>
<td>( 5.1828 \times 10^{-7} )</td>
</tr>
</tbody>
</table>

Much of the data in the table above are not necessary for the solution of this problem. What we need is the value of the load voltage, \( V_L \), as a function of the load current. Assuming a plausible model for the behavior of the cell, we write,

\[
V_L = V_{oc} - R_{\text{int}} I_L - V_{act}. \quad (6)
\]

We omitted transport losses, as specified by the problem statement. Since there is no linear relationship between \( V_L \) and \( I_L \), we discarded the representation of the cell as a simple voltage generator in series with an internal resistance.
We frequently use $V_{act} = V_2 \ln \frac{I_L}{I_0}$. The numerical manipulations that follow are simplified by using the alternative form, $V_{act} = V_1 + V_2 \ln I_L$. In this case, Equation 6 becomes,

$$V_L = V_{oc} - R_{int} I_L - V_1 - V_2 \ln I_L \quad (8)$$

For $I_L = 3$:
$$0.9693 = V_{oc} - 3R_{int} - V_1 - 1.09861V_2 \quad (9)$$

For $I_L = 10$:
$$0.8955 = V_{oc} - 10R_{int} - V_1 - 2.30259V_2 \quad (10)$$

For $I_L = 30$:
$$0.8005 = V_{oc} - 30R_{int} - V_1 - 3.40120V_2 \quad (11)$$

For $I_L = 100$:
$$0.6004 = V_{oc} - 100R_{int} - V_1 - 4.60517V_2 \quad (12)$$

Take Equation 10 and subtract Equation 11:

$$0.8955 = V_{oc} - 10R_{int} - V_1 - 2.30259V_2$$
$$-0.8005 = -V_{oc} + 30R_{int} + V_1 + 3.40120V_2$$

$$0.09500 = 20R_{int} + 1.09861V_2 \quad (13)$$

Take Equation 11 and subtract Equation 12:

$$0.8005 = V_{oc} - 30R_{int} - V_1 - 3.40120V_2$$
$$-0.6004 = -V_{oc} + 100R_{int} + V_1 + 4.60517V_2$$

$$0.20010 = 70R_{int} + 1.20397V_2 \quad (14)$$

Multiply Equation 13 by 1.0959 and subtract Equation 14:

$$0.10411 = 21.9181R_{int} + 1.20397V_2$$
$$-0.20010 = -70R_{int} - 1.20397V_2$$

$$-0.09599 = -48.082R_{int}$$

$$R_{int} = 0.002 \ \Omega. \quad (15)$$
Introduce this value of $R_{int}$ in Equation 14 and solve for $V_2$:

$$V_2 = 0.20010 - 70 \times 0.002 - 0.05 = 0.05 \text{ V.} \quad (16)$$

We have now found the values of two of the four unknowns, $R_{int}$, and $V_2$. It is easy to find the value of $V_{oc} - V_1$. To solve this problem, there is no need to separate them.

We can use Equation 12 (or any other equation of the set). Introducing the values of $R_{int}$ and $V_2$,

$$6.004 = (V_{oc} - V_1) - 0.2 - 0.2303, \quad (17)$$

from which

$$V_{oc} - V_1 = 1.031 \text{ V.} \quad (18)$$

The full equation describing the load voltage of the cell is,

$$V_L = 1.031 - 0.002I_L - 0.05 \ln I_L, \quad (19)$$

and the load power is,

$$P_L = 1.031I_L - 0.002I_L^2 - 0.05I_L \ln I_L \quad (20)$$

Numerically we find that the load power is a maximum of 74 W when the load current is 180 A.

Maximum power output from the cell is obtained at a load current of 180 A and is 74 W.