1. Since the heating takes place at constant pressure, the proper quantity to use is

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{d}{dT}[U+PV] = \frac{d}{dT}\left[\frac{f}{2}Nk_BT + Nk_BT\right] = \left(\frac{f}{2}+1\right)Nk_B$$

We then calculate the flow in terms of number of particles per unit time from

$$E = C_P\Delta T = \left(\frac{f+2}{2}\right)Nk_B\Delta T \quad\Rightarrow\quad \frac{dN}{dt} = \frac{1}{\left(\frac{f+2}{2}\right)k_B\Delta T}\frac{dE}{dt}.$$

Here $dE/dt = 1$ kW is the power of the hair dryer. Then make use of

$$PV = Nk_BT_{\text{out}} \quad\Rightarrow\quad V = \frac{k_BT_{\text{out}}}{P}N,$$

(using $T_{\text{out}} = T_{\text{in}} + \Delta T = 273 + 22 + 25 = 320$ K) which together gives

$$\frac{dV}{dt} = \frac{k_BT_{\text{out}}}{P}\frac{dN}{dt} = \frac{k_BT_{\text{out}}}{P}\frac{1}{\left(\frac{f+2}{2}\right)k_B\Delta T}\frac{dE}{dt} = \frac{2}{f+2}\frac{T_{\text{out}}}{P\Delta T}\frac{dE}{dt}$$

With numbers this becomes

$$\frac{dV}{dt} = \frac{2}{7}\frac{320}{10^5\cdot 25}\cdot 1000 = \frac{2\cdot 320\cdot 10^3}{7\cdot 25\cdot 10^5} \approx 0.0366\text{m}^3/\text{s} \approx 37\ell/\text{s}.$$

2. a) We have the multiplicity

$$\Omega = \binom{N}{n} = \frac{N!}{n!(N-n)!},$$

and the Stirling approximation $\ln x! \approx x\ln x - x$. Together these give (after noting that certain terms cancel each other out),

$$\ln\Omega = N\ln N - n\ln n - (N-n)\ln(N-n)$$

With

$$\ln(N-n) = \ln[N\left(1-\frac{n}{N}\right)] \approx \ln N - \frac{n}{N},$$

this becomes

$$\ln\Omega = N\ln N - n\ln n - N\ln N + n\ln N + n - \frac{n^2}{N} = n\ln\frac{N}{n} + n - \frac{n^2}{N}.$$

With $x = n/N$:

$$\frac{S}{N} = k_B[x\ln x + x - x^2].$$

b) We have $U = \epsilon n - \epsilon(N-n) = \text{const} + 2\epsilon n$. Note also that

$$\frac{1}{N}\frac{\partial S}{\partial x} = \ln\frac{1}{x} - 2x.$$

We then find the temperature

$$T = \frac{\partial U}{\partial S} = \frac{\partial U}{\partial n}\frac{\partial x}{\partial (S/N)} = \frac{2\epsilon}{k_B}/(-\ln x - 2x).$$

c) We get

$$T = \frac{2\times 10^{-28}}{1.38\times 10^{-23}}\frac{1}{\ln 10 - 0.2} = 6.9\mu\text{K}.$$

3. We have $Q = C_V dT$ which leads to

$$S(T) = S(0) + \int_0^T \frac{C_V}{T'}dT' = \int_0^T (a + bT'^2)dT' = aT + \frac{b}{3}T^3.$$

This gives $S(T=10) = 0.0218$ J/K.

4. a) Heat enters at step 2 → 3. Heat leaves in the cooling at step 3 → 1. The isotherm should be close to (well, not altogether different from) a $1/V$ curve. Step 3 → 1 should be a vertical line.

b) We have an adiabatic compression which should leave $PV^\gamma = PVV^{\gamma-1} \propto TV^{\gamma-1}$ constant. Therefore

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}, \quad\Rightarrow\quad T_1 = T_2(V_2/V_1)^{\gamma-1}.$$

1 → 2 The adiabatic process gives

$$Q_{12} = 0.$$

Using

$$PV^\gamma = P_2V_2^\gamma \Rightarrow P = P_2V_2^\gamma V^{-\gamma} = Nk_BT_2V_2^{\gamma-1}V^{-\gamma}$$

we have

$$\begin{aligned} W_{12} &= -\int P(V)dV = -Nk_BT_2V_2^{\gamma-1}\int_{V_1}^{V_2} V^{-\gamma}dV \\ &= \frac{Nk_BT_2V_2^{\gamma-1}}{\gamma-1}\left[V^{1-\gamma}\right]_{V_1}^{V_2} = \frac{Nk_BT_2V_2^{\gamma-1}}{\gamma-1}\left(V_2^{1-\gamma} - V_1^{1-\gamma}\right) \\ &= \frac{Nk_BT_2}{\gamma-1}\left[1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}\right]. \end{aligned}$$

A simpler way to get an equivalent result is through $\Delta U = W + Q$ and $Q = 0$ which gives

$$W_{12} = \Delta U = U_2 - U_1 = \frac{f}{2} N k_B (T_2 - T_1).$$

$2 \to 3$

$$W_{23} = -\int_{V_2}^{V_1} P(V)dV = -Nk_B T_2 \int_{V_2}^{V_1} \frac{dV}{V} = -Nk_B T_2 \ln(V_1/V_2),$$

and $Q_{23} = -W_{23} = Nk_B T_2 \ln(V_1/V_2)$.

$3 \to 1$ Constant volume:

$$W_{31} = 0.$$

$$Q_{31} = \Delta U = \frac{f}{2} N k_B (T_1 - T_2) = -\frac{f}{2} N k_B T_2 \left(1 - \frac{T_1}{T_2}\right).$$

c) We now have $Q_h = Q_{23}$, $Q_c = -Q_{31}$, and $W_e = Q_h - Q_c$. The efficiency becomes

$$\begin{aligned} \epsilon &= \frac{W_e}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{\frac{f}{2}(1 - T_1/T_2)}{\ln(V_1/V_2)} = 1 - \frac{(1 - (V_2/V_1)^{\gamma-1})}{\frac{2}{f}\ln(V_1/V_2)} \\ &= 1 - \frac{1 - 1/X}{\ln X} = 1 - \frac{1}{X}\frac{X-1}{\ln X} \end{aligned}$$

d) Note that the Carnot efficiency is $\epsilon = 1 - T_c/T_h = 1 - T_1/T_2 = 1 - 1/X$. To show that the efficiency is lower is to show that $\frac{X-1}{\ln X} > 1$.
Since $\ln(x+1) \approx x - x^2/2$ we have $\ln X \approx (X-1) - (X-1)^2/2$. We therefore have

$$\frac{X-1}{\ln X} \approx \frac{X-1}{(X-1) - (X-1)^2/2},$$

and since the denominator is smaller than the numerator this is clearly > 1.

5. We have

$$dG_\ell = -S_\ell dT + V_\ell dP, \quad dG_g = -S_g dT + V_g dP.$$

Along the phase boundary we have $dG_g = dG_\ell$ and we may therefore write

$$-S_\ell dT + V_\ell dP = -S_g dT + V_g dP.$$

After rearranging we get

$$(S_g - S_\ell)dT = (V_g - V_\ell)dP \quad \Rightarrow \frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V},$$

since the latent heat is $L = T\Delta S$.

6. Using $\Delta V = V_{\text{gas}} - V_{\text{liq}} \approx V_{\text{gas}} = nRT/P$ in Clausius-Clapeyron's equation gives

$$L = \frac{dP}{dT} T\Delta V = \frac{dP}{dT} T \frac{nRT}{P} = \frac{1}{P}\frac{dP}{dT}\, nRT^2.$$

From the table we estimate

$$\left.\frac{dP}{dT}\right|_{70} \approx \frac{P(75) - P(65)}{75 - 65} = \frac{0.3855 - 0.2501}{10} = 0.01354 \text{ bar/K}.$$

One mole of water has the weight 18g and one kg of water is therefore

$$n = \frac{1000}{18} \text{ mole}.$$

Taken together this becomes

$$L = \frac{1}{P(70)}\frac{dP}{dT}\, nRT^2 = 2.36 \times 10^6 \text{ J/kg}.$$

This is just slightly bigger than the latent heat at 100°C which is 2.26×10^6 J/kg. [Additional note: The curve $P(T)$ is far from linear and one can worry about the precision in the determination of dP/dT. That can however be improved by noting that

$$\frac{1}{P}\frac{dP}{dT} = \frac{d\ln P}{dT} \quad \to \quad \frac{\ln P(75) - \ln P(65)}{75 - 65},$$

which is better since $\ln P$ is almost linear in T. The difference in the result is however small; using this method one gets $L = 2.35 \times 10^6$ J/kg.]

7. a) We have

$$\begin{aligned}\Delta H &= H_{\text{out}} - H_{\text{in}} = 2 \times (-285.83) + (-393.51) - [-74.81 - 2 \times 0] = \\ &= -890.36 \approx -890 \text{ kJ},\end{aligned}$$

and

$$\begin{aligned}\Delta G &= G_{\text{out}} - G_{\text{in}} = 2 \times (-237.13) + (-394.36) - [-50.72 - 2 \times 0] = \\ &= -817.90 \approx -818 \text{ kJ},\end{aligned}$$

   b) $W \geq \Delta G \Rightarrow W \geq -818$ kJ. Negative sign means that work is done by the fuel cell.

   c)

8. (a) Fig for T_5 is for 90.2 K and figure for T_1 is for 77.4 K. At these temperatures the free energies for liquid and gas are the same for pure oxygen and pure nitrogen, respectively.

   (b) T_1 is the lowest temperature which follows from part (a). Solid line corresponds to liquid, which is clear from the figure at the lowest temperature where the liquid should have the lowest free energy.

   (c) It is the figure with temperature T_3. Zooming in and making a dashed vertical line for 21% oxygen one sees that the free energy along the blue line between $x \approx 0.18$ and $x \approx 0.48$ gives a lower free energy than from the solid line for gas only. The liquid that forms will have about 50% oxygen. (I do of course not expect you to "zoom in", but this is only to try to explain better.)

9. a) $\mu_{\text{H}_2} + 3\mu_{\text{N}_2} = 2\mu_{\text{NH}_3}$.

   b) *This solution follows rather directly from the text book.*