ChE-304 Problem Set 4

Week 4

Problem 1

Massieu (a French mathematician and physicist) proposed alternate thermodynamic potentials based on entropy as a function of internal energy ($dS(U,V,N)$). We don't use them because they are less practical than the ones you are used to seeing. Can you write the 4 "Massieu thermodynamic potentials" with dS being the first and the 3 others obtained using Legendre transformations?

Hint: the goal of the Legendre transforms is to have the variables be functions of intensive variables (in this case T and P). They do not have to be as simple as the classical potentials you are used to.

Solution

$$dU = TdS - PdV + \mu dN \rightarrow dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$$

This is the first Massieu function and S is the first thermodynamic potential.

To find the others, we want functions that vary with intensive variables (T and P) rather than extensive variables.

With: $d\left(\frac{U}{T}\right) = Ud\left(\frac{1}{T}\right) + \frac{1}{T}dU$

We can write:

$$dS = d\left(\frac{U}{T}\right) - Ud\left(\frac{1}{T}\right) + \frac{P}{T}dV - \frac{\mu}{T}dN \rightarrow d\left(S - \frac{U}{T}\right) = -Ud\left(\frac{1}{T}\right) + \frac{P}{T}dV - \frac{\mu}{T}dN$$

This is the 2nd Massieu function and $S - \frac{U}{T}$ is the 2nd thermodynamic potential.

Now let's use $d\left(\frac{PV}{T}\right) = \frac{P}{T}dV + Vd\left(\frac{P}{T}\right)$

$$dS = \frac{dU}{T} + d\left(\frac{PV}{T}\right) - Vd\left(\frac{P}{T}\right) - \frac{\mu}{T}dN \rightarrow d\left(S - \frac{PV}{T}\right) = \frac{dU}{T} - Vd\left(\frac{P}{T}\right) - \frac{\mu}{T}dN$$

This is the 3rd Massieu function and $S - \frac{PV}{T}$ is the 3rd thermodynamic potential.

The 4th Massieu function is a combination of the 2:

$$d\left(S-\frac{U}{T}-\frac{PV}{T}\right)=-Ud\left(\frac{1}{T}\right)-Vd\left(\frac{P}{T}\right)-\frac{\mu}{T}dN$$

Where $S-\frac{U}{T}-\frac{PV}{T}$ is the 4th thermodynamic potential.

Problem 2

The Petit Chêne in Lausanne goes up by about 60 m. Imagine you want to build a 1 ton car that can go up the Petit Chêne in one minute. Assuming the only thing the car has to deal with is climbing the hill (no friction, or other non ideal losses) and that the fuel cell is reversible, what are the minimum number of hydrogen fuel cells you will need and the minimum hydrogen consumption per time?

Assume a typical fuel cell current densities are on the order of 1 A/cm^2 with reasonably sized cell that can fit into a car (measuring 100 cm^2).

Faraday's constant: $F = 96485 \frac{C}{mol\, e^{-¿}¿}$

Solution

$$Mech.\,Power = \frac{mg\Delta z}{t} = 1000\,9.8\,1\,1 = 9'800\,J/S$$

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}} = \frac{-237}{-286} = 83\,\%$$

$$HHV_{H_2} = 142\frac{MJ}{kg} \rightarrow H_2 consumption = \frac{9'800\frac{J}{S}}{0.83\frac{142'000\,J}{g}}\frac{60\,sec}{min} = 5.0\,g_{H2}/min$$

$$P_{electric} = n_{fuelCells}E_0 I \rightarrow n_{fuelCells} = \frac{P_{electric}}{E_0 I}$$

$$E_0 = \frac{-\Delta G^0_{RXN,H_2}}{nF} = \frac{237'000}{296'485} = 1.23V$$

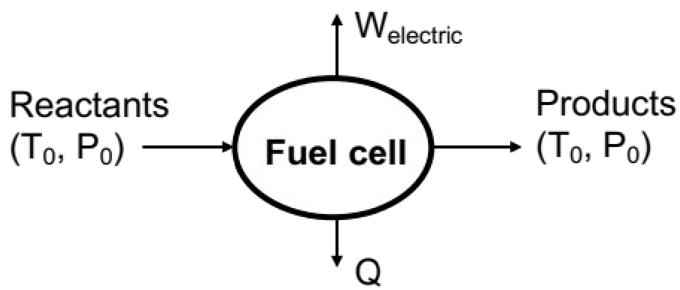
$$n_{fuelCells} = \frac{9'800\frac{J}{S}}{1.23\,100} = 80$$

The real number for a typical car is close to 400… but this simple calculation gets us close.

Problem 3

Can you re-derive the efficiency of a fuel cell using a simple energy balance for a reversible fuel cell? Assume reactants enter the fuel cell continuously and products (after full reaction) exit the fuel cell continuously. Draw all the incoming and exiting energy streams and write the energy balance.

Solution:



Doing a simple energy balance:

In – Out = Acc

Since we are in a continuous system, we can use enthalpy to account for the energy released by the transformation from reactants to products:

$$\dot{m}_{reactants} H_{reactants}(T_0, P_0) - \dot{m}_{products} H_{products}(T_0, P_0) - \dot{Q} - \dot{W}_{electric} = 0$$

Since there is no accumulation of mass in the fuel cell, we have $\dot{m}_{reactants} = \dot{m}_{products} = \dot{m}$:

$$\dot{m}(-\Delta H_{RXN}(T_0, P_0)) = \dot{Q} + \dot{W}_{electric}$$

In an ideal case, $\dot{Q} = -\dot{Q}_{rev}$ (we add a negative sign because Q_{rev} is always calculated from the systems perspective, while in the energy balance we already assumed that it was exiting the system)

$$\dot{m}(-\Delta H_{RXN}(T_0, P_0)) = -\dot{Q}_{rev} + \dot{W}_{electric}$$

From the definition of Q_{rev}: $\frac{dQ_{rev}}{T} = dS$

Here, everything is isothermal, so we assume Q_{rev} is released at T_0:

$$\frac{dQ_{rev}}{T_0} = dS(T_0, P_0)$$

$$\dot{Q}_{rev} = \dot{m} T_0 \int dS(T_0, P_0) = \dot{m} T_0 \left(S_{products}(T_0, P_0) - S_{reactants}(T_0, P_0) \right) = \dot{m} T_0 \Delta S_{RXN}(T_0, P_0)$$

From the expression above:

$$\dot{m}\left(-\Delta H_{RXN}(T_0, P_0)\right) = -\dot{m} T_0 \Delta S_{RXN}(T_0, P_0) + \dot{W}_{electric}$$

$$\dot{W}_{electric} = \dot{m}\left(-\Delta H_{RXN}(T_0, P_0) + T_0 \Delta S_{RXN}(T_0, P_0)\right) = \dot{m}\left(-\Delta G_{RXN}(T_0, P_0)\right)$$

$$\eta = \frac{\dot{W}_{electric}}{\dot{m}_{reactants} H_{reactants}(T_0, P_0) - \dot{m}_{products} H_{products}(T_0, P_0)} = \frac{\dot{m}\left(-\Delta G_{RXN}(T_0, P_0)\right)}{\dot{m}\left(-\Delta H_{RXN}(T_0, P_0)\right)} = \frac{-\Delta G_{RXN}(T_0, P_0)}{-\Delta H_{RXN}(T_0, P_0)}$$

In this balance it’s easy to see how, if $\Delta S_{RXN}(T_0, P_0)$ is positive, the system would in fact be receiving extra heat from the surroundings, which would then need to be included in the inputs for the efficiency calculation.