

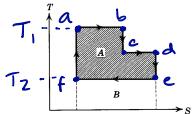
HW #1 Solutions

Problems:
#1.2, 1.4, 1.5

1.2

1.2 (a) An engine is represented by the cyclic transformation shown in the accompanying $T-S$ diagram, where A denotes the area of the shaded region and B the area of the region below it. Show that this engine is not as efficient as a Carnot engine operating between the highest and the lowest available temperatures.

(b) Show that an arbitrary reversible engine cannot be more efficient than a Carnot engine operating between the highest and the lowest available temperatures.



a) For a cyclic engine we know that

$$dU = dQ - dW = 0$$

$$\Rightarrow dQ = dW$$

We are concerned about the efficiency of this engine, which is defined by

$$\eta = \frac{W}{Q_{\text{abs}}} \quad \text{where } Q_{\text{abs}} \text{ is the heat absorbed by the system}$$

$$\text{Recall that } dQ = T dS$$

$$\Rightarrow W_{\text{tot}} = \oint dW = \oint dQ = \oint T dS \\ = A$$

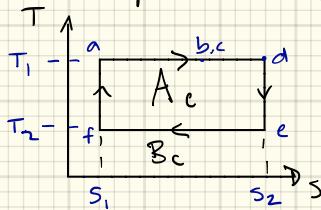
If we consider the cycle going from $a \rightarrow b \rightarrow c \rightarrow d \rightarrow e \rightarrow f$, then we notice that heat is only absorbed from $a \rightarrow b$ & $c \rightarrow d$.

Integrating from state a to state d

$$Q_{\text{abs}} = \int_a^d T dS = A + B$$

$$\Rightarrow \boxed{\eta = \frac{A}{A+B} = \frac{1}{1+B/A}}$$

If we created a Carnot engine that also operated between the temperatures $T_1 > T_2$, then a T-S plot would look like



We see that $A_c > A$ & $B_c = B$

$$\therefore \eta_c = \frac{1}{1+B_c/A_c} > \eta$$

- b) The efficiency $\eta = (1+B/A)^{-1}$ does not change for a reversible process. Because the Carnot engine involves two isothermal processes paired with two adiabatic processes, then for two given operating temperatures T_1 & T_2

$$A_c = (S_2 - S_1)(T_2 - T_1)$$

$$B_c = (S_2 - S_1)T_1$$

We can see then that $\eta_c = T_2 - T_1 / T_2 = 1 - T_1 / T_2$

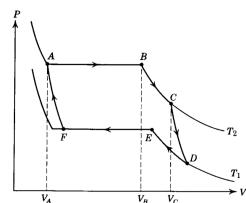
\therefore it only depends on the min & max temperature by minimizing the ratio B/A . Any other cycle will only decrease this ratio & be less efficient.

1.4

Two isotherms of 1 mol of a substance that can undergo a gas-liquid transition are shown in the accompanying $P-V$ diagram. The absolute temperatures are T_2 and T_1 , respectively. The substance is made to go through one cycle of a cyclic reversible transformation $ABCDEF$, as indicated in the diagram. The following information is given:

- (i) ABC and DEF are isothermal transformations.
- (ii) FA and CD are adiabatic transformations.
- (iii) In the gas phase ($BCDE$) the substance is an ideal gas. At A the substance is pure liquid.
- (iv) Latent heat along AB : $L = 200 \text{ cal/mol}$
 $T_2 = 300 \text{ K}$
 $T_1 = 150 \text{ K}$
 $V_A = 0.5 \text{ liter}$
 $V_B = 1 \text{ liter}$
 $V_C = 2.71828 \text{ liter}$

Calculate the net amount of work done by the substance.



We begin by recalling from the previous problem that

$$\eta = \frac{W}{Q_{\text{abs}}} \Rightarrow W = \eta Q_{\text{abs}}$$

Additionally, we first recognize that this is a Carnot engine. As mentioned in Problem (1.2), the efficiency is related to the minimum & maximum operating temperatures of the system

$$\eta = 1 - \frac{T_1}{T_2}$$

$$\Rightarrow W = (1 - \frac{T_1}{T_2}) Q_{\text{abs}}$$

So now we just need to determine how much heat is absorbed by the system.

Heat is absorbed between states $A \rightarrow B$ & $B \rightarrow C$

$Q_{A \rightarrow B}$: This is the most straightforward contribution to compute. As stated by the problem the substance is transitioning from a liquid to gas & its heat is, therefore, given by the latent heat

$$L = 200 \text{ cal/mol}$$

$Q_{B \rightarrow C}$: Now the substance can be approximated by an ideal gas. For an ideal gas

$$dU = 0 = dQ - dW \Rightarrow dQ = dW = PdV$$

For an ideal gas, the equation of state is given by

$$PV = NkT \Rightarrow P(V, T) = \frac{NkT}{V}$$

This is an isothermal process $\therefore T = \text{const} = T_2$

$$\Rightarrow Q_{B \rightarrow C} = \int_B^C dQ = \int_{V_B}^{V_C} \frac{NkT_2}{V} dV = NkT_2 \log(V_C/V_B)$$

$$\therefore Q_{\text{abs}} = Q_{A \rightarrow B} + Q_{B \rightarrow C} = L + RT_2 \log(V_C/V_B)$$

$$\Rightarrow W = (1 - \frac{T_1}{T_2})(L + RT_2 \log(V_C/V_B))$$

2.710281

where I substituted $Nk = nR$ for convenience of the calculation
Plugging in all the appropriate values, we see that

$$W = (1 - \frac{150 \text{ kJ}/300 \text{ K}}{(200 \text{ cal} + (1.99 \text{ cal/K})(300 \text{ K}) \log(\frac{2710281}{1}))} \approx 400 \text{ cal}$$

1.5

1.5 A substance has the following properties:

- (i) At a constant temperature T_0 the work done by it on expansion from V_0 to V is

$$W = RT_0 \log \frac{V}{V_0}$$

- (ii) The entropy is given by

$$S = R \frac{V}{V_0} \left(\frac{T}{T_0} \right)^a$$

where V_0 , T_0 , and a are fixed constants.

- (a) Calculate the Helmholtz free energy.
 (b) Find the equation of state.
 (c) Find the work done at an arbitrary constant temperature T .

a) We first need to derive Maxwell relations to relate S & W to the Helmholtz free energy. So first consider

$$\begin{aligned} A = U - TS &\Rightarrow dA = dU - TdS - SdT \\ &= -SdT - dW \\ \Rightarrow \left(\frac{\partial A}{\partial W} \right)_T &= -1 \quad \boxed{1} \quad \text{&} \quad \left(\frac{\partial A}{\partial T} \right)_W = -S \quad \boxed{2} \end{aligned}$$

So by integrating our equations for W & S , we can solve for A . Let's begin w/ our equation for W

$$W = RT_0 \log \left(\frac{V}{V_0} \right)$$

From Eqn. $\boxed{1}$, we quickly see that, for T held constant @ T_0

$$A(V, T_0) = -RT_0 \log \left(\frac{V}{V_0} \right) \quad \boxed{A}$$

To solve for the temperature dependence, we take our equation for S

$$S = R \frac{V}{V_0} \left(\frac{T}{T_0} \right)^a \quad \boxed{3}$$

Using Eqns $\boxed{2}$ & $\boxed{3}$, & holding V const.

$$A(V, T) = -\frac{RT_0}{a+1} \frac{V}{V_0} \left(\frac{T}{T_0} \right)^{a+1} + C(V) \quad \boxed{B}$$

where $C(V)$ is a constant of integration that can depend on V , since V was held constant for our integration

We can solve for $C(V)$ by taking Eqn B and setting $T=T_0$ & comparing to Eqn. A

$$A(V, T_0) = -RT_0 \log(V/V_0) = -\frac{RT_0}{a+1} \left(\frac{V}{V_0}\right)^{a+1} + C(V)$$

$$\Rightarrow C(V) = -RT_0 \log(V/V_0) + \frac{RT_0}{a+1} \frac{V}{V_0}$$

$$\therefore A(V, T) = \frac{RT_0}{a+1} \frac{V}{V_0} \left[1 - \left(\frac{T}{T_0} \right)^{a+1} \right] - RT_0 \log \left(\frac{V}{V_0} \right)$$

b) Return to the differential form of the Helmholtz free energy and replace $dW = PdV$

$$dA = -SdT - PdV$$

Then we see that $-P = \left(\frac{\partial A}{\partial V}\right)_T$

$$\therefore P = -\frac{RT_0}{a+1} \frac{1}{V_0} \left[1 - \left(\frac{T}{T_0} \right)^{a+1} \right] + \frac{RT_0}{V}$$

c) Finally, we look to calculate the work for a constant temp T by simply integrating our answer from part (b)

$$W = \int PdV$$

$$W = -\frac{RT_0}{a+1} \frac{\Delta V}{V_0} \left[1 - \left(\frac{T}{T_0} \right)^{a+1} \right] + RT_0 \log \left(\frac{V_f}{V_i} \right)$$

where V_f is the final state volume & V_i is the initial state volume
 $\& \Delta V \equiv V_f - V_i$

$$\Rightarrow W = A(V_i, T) - A(V_f, T)$$

$$W = -\Delta A$$