

PHY252 PS3 — 03/25/2022

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Q1.

(a) Given that $U = 3nRT$, we wish to find the entropy S , the enthalpy H , the Helmholtz free energy F and the Gibbs free energy G . Since we can treat $CH_4(g)$ as an ideal gas, we can invoke the ideal gas law, $PV = nRT$.

By definition,

$$\begin{array}{lll} H = U + PV & F = U - TS & G = U + PV - TS \\ = 3nRT + nRT & = 3nRT - TS & = 3RT + nRT - TS \\ = 4nRT & = 3nRT - TS & = 4nRT - TS \end{array}$$

From the back of the textbook, each of the values are given for one mole of the substance at $298K = 25^\circ C$. The given value of entropy of CH_4 at $298K$ is $S = 186.26 J/K$. Taking $T = 298K$, $n = 1$, and $R = 8.3145 Jmol^{-1}K^{-1}$, then

$$\begin{aligned} H &= 4(1mol)(8.3145 Jmol^{-1}K^{-1})(298K) \\ &= 9.91 \times 10^3 J \\ F &= 3(1mol)(8.3145 Jmol^{-1}K^{-1})(298K) - (298K)(186.26 JK^{-1}) \\ &= -48.1 \times 10^3 J \\ G &= 4(1mol)(8.3145 Jmol^{-1}K^{-1})(298K) - (298K)(186.26 JK^{-1}) \\ &= -45.6 \times 10^3 J. \end{aligned}$$

Therefore for one mole of methane at room temperature and atmospheric pressure,

$S = 186.26 J/K$	$H = 9.91 kJ$	$F = -48.1 kJ$	$G = -45.6 kJ.$
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(1b) To find the change in Gibbs free energy, we must consider the change in entropy to be negligible over $3 K$:

$$\left(\frac{\partial G}{\partial T} \right)_{P,N} = -S \implies \Delta G = 4nR\Delta T + S\Delta T.$$

Taking $\Delta T = T_f - T_i = 301K - 298K = 3K$, $n = 1 mol$ and $R = 8.3145 Jmol^{-1}K^{-1}$, the change in the Gibbs free energy is $\Delta G = 4(1 mol)(8.3145 Jmol^{-1}K^{-1})(3 K) - (186.26 J/K)(3 K) = -459.006 J$. Therefore

$\Delta G = -459 J.$

(1c) To find the change in enthalpy ΔH and the Gibbs free energy ΔG for one mole of each species in the reaction, we can invoke the relation between the energy of the reactants and the products:

$$\Delta H = \Delta_f H_{products} - \Delta_f H_{reactants} \quad \Delta G = \Delta_f G_{products} - \Delta_f G_{reactants}.$$

From the back of the textbook, we have that

$\Delta_f G(kJ) :$	$CH_4 : -50.72$	$\Delta_f H(kJ) :$	$CH_4 : -74.81$
	$O_2 : 0$		$O_2 : 0$
	$H_2O : -228.57$		$H_2O : -241.82$
	$CO_2 : -394.36$		$CO_2 : -393.51.$

Then, in kJ ,

$$\Delta H = [2(-241.82) + (-393.51)] - [(-74.81) + 2(0)] = -802.34 \text{ kJ}$$

and

$$\Delta G = [2(-228.57) + (-394.36)] - [(-50.71) + 2(0)] = -800.79 \text{ kJ}.$$

Therefore the change in enthalpy and Gibbs free energy for this reaction are

$\Delta H = -802 \text{ kJ} \quad \text{and} \quad \Delta G = -800 \text{ kJ}.$

(1d) Under constant pressure, the change in enthalpy per mole is equivalent to the amount of heat produced per mole: $\Delta H = Q$. Therefore the heat produced per mole of methane is $Q = -802 \text{ kJ}$, so heat is absorbed throughout the reaction process.

Q2.

(a) By definition, the efficiency of the engine is given by $e = 1 - \frac{Q_T}{Q_H}$. I will begin by calculating the work done along each of the four stages of the engine cycle, since $-Q = W$. Since the heat absorbed is just $-Q_H = W_B$, then efficiency is given by

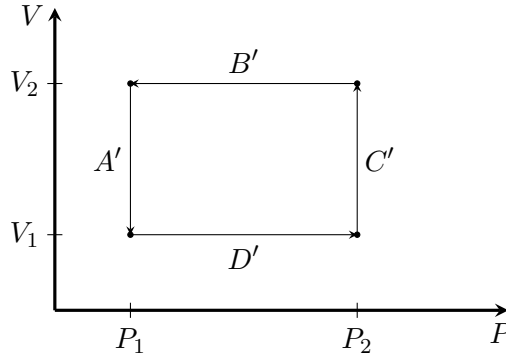
$$e = \frac{W_A + W_B + W_C + W_D}{W_B}.$$

Since the work done along stages A and C is zero because the volume change is zero, then the efficiency is $e = 1 + \frac{W_D}{W_B}$. Now

$$\begin{aligned} W_D &= P_1(V_1 - V_2) & W_B &= P_2(V_2 - V_1) \\ &= P_1(V_1 - 5V_1) & &= 3P_1(5V_1 - V_1) \\ &= -4P_1V_1 & &= 12P_1V_1. \end{aligned}$$

This implies that $e = 1 + \frac{-4P_1V_1}{12P_1V_1} = 1 - \frac{1}{3} = \frac{2}{3}$. Therefore the efficiency is $\boxed{e = \frac{2}{3}}$.

(2b) In reverse, the cycle is



In an ideal engine, the gas must be able to absorb heat throughout stages A and B . This is a direct result of the ideal gas law $PV = nRT$, since if either P or V increase, T must increase proportionally. Then the engine will release heat throughout steps C and D . Equivalently, in the reverse cycle shown above, the gas must absorb heat through reverse stages D' and C' and release heat during the B' and A' stages.

By the ideal gas law, the temperature of the gas is directly proportional to PV , so the temperature of the gas continuously changes through the cycle. However, this means that the gas will absorb heat throughout the range of temperatures over the stages D' and C' , then release heat over the same range of temperatures due to the symmetry of the cycle along stages B' and A' . If the cycle absorbs heat from the inside of the fridge (the cold reservoir) and continues to absorb heat

over each cycle, then this implies that the cold reservoir (inside of the fridge) is much hotter than the gas itself, since the gas can continue to absorb heat. Likewise, if all the released heat goes into the hot reservoir (the kitchen), then the temperature of the kitchen will always be colder than the gas ever gets.

This is why this cycle cannot work in reverse for refrigeration.

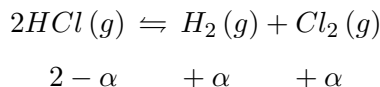
(2c) By the symmetry of the cycle, the extremes of the temperature is $T_1 = \frac{P_1 V_1}{nR}$ (lowest temperature), and $T_2 = \frac{P_2 V_2}{nR} = \frac{15P_1 V_1}{nR}$ (hottest temperature). The efficiency of an ideal engine is given by

$$e \leq 1 - \frac{T_C}{T_H} \implies e_{max} = 1 - \frac{T_C}{T_H},$$

which is then just $e = 1 - \frac{P_1 V_1 / nR}{15P_1 V_1 / nR} = 1 - \frac{1}{15} = \frac{14}{15}$, which is quite efficient. Therefore the efficiency of an ideal engine operating at the same temperature extremes is about $e = 93\%$.

Q3.

(a) If we begin with 2 moles of HCl , then the extent α is simply



The partial pressure of each species are given by $P_i = \frac{N_i}{N_{tot}} P_{tot}$. The value N_i is the number of particles of a species, which, in terms of the extent, is $\alpha n_{tot} N_A$. Since $N_{tot} = n_{tot} N_A$, then the partial pressures are just

$$\boxed{P_{HCl} = (2 - \alpha)P_{tot}, \quad P_{H_2} = \alpha P_{tot}, \quad \text{and} \quad P_{Cl_2} = \alpha P_{tot}.}$$

(3b) By the law of mass action, we have that

$$K = \frac{[P_{HCl}]^2 [P_0]^{2-1-1}}{[P_{H_2}]^1 [P_{Cl_2}]^1} = \frac{(2 - \alpha)^2 P_{tot}^2 (1)}{\alpha^2 P_{tot}^2} = \frac{(2 - \alpha)^2}{\alpha^2}.$$

Given that $\alpha = 1.0 \times 10^{-6}$, the value of the equilibrium constant is simply

$$K = \frac{(2 - 1.0 \times 10^{-6})^2}{(1.0 \times 10^{-6})^2} = 3.999996 \times 10^{12}.$$

After rounding, the constant just becomes $\boxed{K = 4 \times 10^{12}}.$

(3c) The standard Gibbs energy, in terms of the equilibrium constant, is

$$\Delta G^o = RT \log \left(\frac{1}{K} \right) = RT \log \left(\frac{\alpha^2}{(2 - \alpha)^2} \right).$$

Again taking $\alpha = 1.0 \times 10^{-6}$, and $T = 900 \text{ K}$, again the the gas constant being $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$, then the standard Gibbs for this reaction is

$$\Delta G = (R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(900 \text{ K}) \log \left(\frac{(1.0 \times 10^{-6})^2}{(2 - 1.0 \times 10^{-6})^2} \right) = -217'138 \text{ J}.$$

To futher simplify, then $\boxed{\Delta G^o = -2.2 \times 10^5 \text{ J}}.$

Q4.

(a) We wish to find the rate at which the excess heat Q_C is expelled into the environment. The work done by the plant is the difference in the expelled heat with the input heat, that is $W = Q_H - Q_C$. By definition, the efficiency of the plant is defined as the work upon the cost, that is $e = 1 - \frac{Q_C}{Q_H}$. At maximum efficiency, we have the relation that $\frac{T_C}{T_H} = \frac{Q_C}{Q_H}$, which implies that $Q_H = \frac{T_H}{T_C} Q_C$. The expression for the work done is then

$$W = \frac{T_H}{T_C} Q_C - Q_C = Q_C \left(\frac{T_H}{T_C} - 1 \right).$$

The output power, which is $\frac{W}{\Delta t}$, is then $P = \frac{Q_C}{\Delta t} \left(\frac{T_H}{T_C} - 1 \right)$. Rearranging to solve for $\frac{Q_C}{\Delta t}$ gives the expression for the amount of heat released by the turbine:

$$\frac{Q_C}{\Delta t} = P \left(\frac{T_H}{T_C} - 1 \right)^{-1}.$$

Taking $T_H = 600^\circ C = 873 K$, $T_C = 30^\circ C = 303 K$ and $P = 5 \times 10^8 W$, then

$$\frac{Q_C}{\Delta t} = (5 \times 10^8 W) \left(\frac{873 K}{303 K} - 1 \right)^{-1} = 265'921'052 W.$$

Therefore the plant expels heat at a rate of $\boxed{\frac{Q_C}{\Delta t} = 2.7 \times 10^8 W.}$

(4b) To find a relationship between heat and temperature, we can consider the specific heat capacity of the water: $c = \frac{Q}{m\Delta T} = 4.186 \times 10^3 J(K \cdot kg)^{-1}$. As the water flows at $80 m^3/s$, with a density of $997 kg m^{-3}$, then every second, $\left[\frac{80 m^3}{s} \right] \times \left[\frac{997 kg}{m^3} \right] = 79'760 kg/s$ passes through a section of the river as a flux. Rearranging the specific heat capacity to solve for the change in temperature ΔT ,

$$\Delta T = \frac{Q_C/\Delta t}{m/\Delta t \cdot c}.$$

Taking $Q_C/\Delta t = 265'921'052 W$ from the previous question (4a), $c = 4.186 \times 10^3 J(K \cdot kg)^{-1}$ and $m/\Delta t = 79'760 kg/s$, then the change in temperature of the river is

$$\Delta T = \frac{265'921'052 W}{(79'760 kg/s)(4.186 \times 10^3 J(K \cdot kg)^{-1})} = 0.7964 K.$$

Therefore the change in the river temperature is $\boxed{\Delta T = 0.8 K.}$

(4c) If the plant expels heat at a rate of $2.7 \times 10^8 W$, then the rate at which water must be evaporated is simply the rate at which heat is expelled upon the latent heat per kilogram required to evaporate the water, that is

$$\text{rate} = \frac{Q_C/\Delta t}{L}.$$

Taking $Q_C/\Delta t$ from question (3a), and $L = 2400 J/g = 2.4 \times 10^6 J/kg$, then the rate required to evaporate the river water is

$$\text{rate} = \frac{265'921'052 J/s}{2.4 \times 10^6 J/kg} = 110.8 kg/s.$$

That is, $\text{rate} = 110 J/K$.

(4d) To find the new amount of power generated, we can invoke the relation between plant efficiencies and powers:

$$\frac{P_{old}}{e_{old}} = \frac{P_{new}}{e_{new}} \implies P_{new} = \frac{P_{old}}{e_{old}} \cdot e_{new}.$$

The old maximum efficiency is given when $T_h = 600^\circ C = 873 K$ and the new efficiency is given when $T_h = 650^\circ C = 923 K$. With $T_C = 303 K$ remaining the same, the new power generated is then

$$P_{new} = \frac{5 \times 10^8 W}{1 - \frac{303 K}{873 K}} \cdot \left(1 - \frac{303 K}{923 K}\right) = 514'398'129 W.$$

Taking the difference between the previous input power, $P_{new} - P_{old} = 514'398'129 W - 5 \times 10^8 W = 14'398'129 W$. Therefore the additional power generated is $P = 1.4 \times 10^7 W$.

(4e) To find the efficiency of this rankine cycle, we require the enthalpies only from stages 1, 3, and 4. This is because $H_1 \approx H_2$ since the pump adds very little energy to the water during this stage. Then the efficiency is given by

$$e = 1 - \frac{H_4 - H_1}{H_3 - H_1}.$$

With the maximum temperature of the steam being $300^\circ C$ at $P = 10$ bars and the lowest temperature released being $30^\circ C$, then by table 4.1 and 4.2, we can deduce that

$$H_1 = 126 kJ \quad \text{and} \quad H_3 = 3051 kJ \text{ with } S_3 = 7.123 kJ/K.$$

I will need S_3 to determine H_4 . This is because during stage 3, the adiabat, $Q = 0$ so the entropy shouldn't change. This gives that $S_4 = S_3 = 7.123 \text{ kJ/K}$. Now, we can use table 4.1 again to interpolate the percentages of steam and water in this phase.

At 30°C , the entropy of water is 0.437 kJ/K , while the entropy of steam is 8.453 kJ/K . To find the percentage of steam, we have that

$$\begin{aligned} S_4 &= 0.437(1 - x) + 8.453x = 7.123 \text{ kJ/K} \\ \implies x_{\text{steam}} &= 0.8341 \dots \end{aligned}$$

With this, the percentage of water is $x_{\text{water}} = 0.1659$ at the 4 stage.

Multiplying these percentages through the values in table 4.1 at 30°C , we have that the enthalpy of the steam is $0.8341 \cdot 2556 \text{ kJ} = 2'131.96 \dots \text{ kJ}$, and the enthalpy of the water is $0.1659 \cdot 126 \text{ kJ} = 20.90 \dots \text{ kJ}$. Adding these together gives the enthalpy at point 4: $H_4 = 2'152.86 \text{ kJ}$. We can now calculate the efficiency:

$$e = 1 - \frac{2'152.86 \text{ kJ} - 126 \text{ kJ}}{3051 \text{ kJ} - 126 \text{ kJ}} = 0.30705.$$

Therefore the efficiency of the plant is $e = 31\%$.

Q5.

(a) We can begin by expressing the total energy U as a function of the volume V and temperature T . Similarly with volume, we can assume that the volume is a function of the pressure P and the temperature T (this is a result of $PV = nRT$ for an ideal gas). It follows that we can expand U and V in terms of its partial derivatives:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (5.1)$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP. \quad (5.2)$$

With the volume kept at constant pressure, $dP \rightarrow 0$. We can substitute equation (5.2) into (5.1) with the expression for dV and $dP = 0$, hence rewriting the energy as

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P dT \implies \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P. \quad (5.3)$$

From the definition of heat capacity at constant volume, we have that $C_V = \left(\frac{\partial U}{\partial V}\right)_T$, which can be substituted into (5.3) to yield

$$\left(\frac{\partial U}{\partial T}\right)_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P. \quad (5.4)$$

Now, the definition of heat capacity at constant pressure is defined in terms of the enthalpy:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial(U + PV)}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P. \quad (5.5)$$

Since (5.4) gives an expression for $\left(\frac{\partial U}{\partial T}\right)_P$, we can substitute (5.4) into equation (5.5) to give that

$$C_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P,$$

which directly implies that $C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right]$, as required. (5.6)

(5b) We begin by deriving a relation between pressure in terms of a partial derivative of the Helmholtz free energy F . By the thermodynamic identities,

$$dU = T dS - P dV \quad (5.7)$$

$$dF = dU - T dS - S dT. \quad (5.8)$$

substituting (5.7) into (5.8) quickly yields that $dF = -S dT - P dV$. However, with temperature held constant as stated, $dT \rightarrow 0$, thus implying that

$$P = - \left(\frac{\partial F}{\partial V} \right)_T \quad (5.9)$$

Expressing pressure in this fashion and writing it into equation (5.6), we have that

$$C_P - C_V = \left(\frac{\partial V}{\partial T} \right)_P \left[\left(\frac{\partial U}{\partial V} \right)_T - \left(\frac{\partial F}{\partial V} \right)_T \right]. \quad (5.10)$$

Helmholtz free energy states $F = U - TS$, so differentiating with respect to volume $\frac{\partial F}{\partial V}$ gives

$$\left(\frac{\partial U}{\partial V} \right)_T - \left(\frac{\partial F}{\partial V} \right)_T = \left(\frac{\partial U}{\partial V} \right)_T - \left(\frac{\partial U}{\partial V} \right)_T + T \left(\frac{\partial S}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T \quad (5.11)$$

and therefore (5.6) and (5.11) imply that

$$\boxed{C_P = C_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P}.$$

(5c) The Maxwell relation we wish to employ is

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V. \quad (5.12)$$

The relation between C_P and C_V is a direct result of (5.11) and (5.12):

$$\boxed{C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P}.$$