Problem set 4 - Solutions

November 20, 2008

1

In this problem, we will assume that the substances obey the Ideal gas law, however they have the unique property that the heat capacities of the gaseous and liquid forms are given by:

$$C_p^g = a' + b'T \qquad C_p^l = a + bT \tag{1}$$

as opposed to the expected form of the heat capacity for an Ideal gas. The expression for the Enthalpy of each of these phases is given by:

$$\begin{aligned} \overline{H} &= \int dT C_p(T) \\ &= \int dT(a + bT) \\ &= aT + \frac{b}{2}T^2 + c \end{aligned}$$

So for the two phases we have:

$$\overline{H}^g = a'T + \frac{b'}{2}T^2 + c' \qquad \overline{H}^l = aT + \frac{b}{2}T^2 + c \tag{2}$$

To find the difference in enthalpy, ΔH, we simply subtract these two functions:

$$\begin{aligned} \Delta H &= \overline{H}^g - \overline{H}^l \\ &= (a' - a)T + \frac{b' - b}{2}T^2 + (c' - c) \\ &= AT + BT^2 + C \end{aligned}$$

Where A, B, C, are defined as the coefficients of the equation as written in the second line of the above equation. Using the assumption that this substance obeys the Ideal gas law, we can plug our expression for enthalpy into the integrated form of the Clausius-Clapeyron equation to get:

$$\begin{aligned} \frac{dP}{P} &= \frac{1}{R}\left(AT + BT^2 + C\right)\frac{dT}{T^2} \\ &= \frac{1}{R}\left(\frac{A}{T} + B + \frac{C}{T^2}\right)dT \end{aligned}$$

Integrating both sides:

$$ln\frac{P}{P_0} = \frac{A}{R}lnT + \frac{B}{R}T - \frac{C}{R}\frac{1}{T} + D \tag{3}$$

Where D is a constant of integration.

2

The vapor pressure of a substance obeys the equation:

$$ln\frac{P}{P_0} = A - \frac{B}{T+C} \tag{4}$$

where, $P_0 = 1$.

(a) From the Clausius-Clapeyron equation we have:

$$\frac{dP}{dT} = \frac{\Delta S_{vap}}{\Delta V} \tag{5}$$

So, we differentiate the Clausius-Clapeyron equation in order to get an expression for $\frac{dP}{dT}$.

$$\begin{aligned} ln\frac{P}{P_0} &= A - \frac{B}{T+C} \\ P &= P_0 e^{A-\frac{B}{T+C}} \\ \frac{dP}{dT} &= \frac{B}{(T+C)^2}P_0 e^{A-\frac{B}{T+C}} \\ &= \frac{B}{(T+C)^2}P \end{aligned}$$

rearranging the first equation gives:

$$\begin{aligned} \frac{B}{(T+C)^2}P &= \frac{\Delta S_{vap}}{\Delta V} \\ \Delta S_{vap} &= \frac{P\Delta VB}{(T+C)^2} \end{aligned}$$

(b)
In this problem we will once again assume that $\Delta V \approx V_g$, and that the gas obeys the ideal gas law. So:

$$\begin{aligned} \Delta S_{vap} &= \frac{P\Delta VB}{(T+C)^2} \\ (T+C)^2 &= \frac{PV_gB}{\Delta S_{vap}} \\ T^2 + 2TC + C^2 &= \frac{RBT}{\Delta S_{vap}} \\ T^2 + \left(2C - \frac{RB}{\Delta S_{vap}}\right)T + C^2 &= 0 \end{aligned}$$

This can be solved for T by using the quadratic formula.

$$\begin{aligned} T &= \frac{-\left(2C - \frac{RB}{\Delta S_{vap}}\right) \pm \sqrt{\left(2C - \frac{RB}{\Delta S_{vap}}\right)^2 - 4C^2}}{2} \\ &= \frac{RB \pm \sqrt{4C^2 - \frac{4CRB}{\Delta S_{vap}} + \frac{(RB)^2}{\Delta S_{vap}^2} - 4C^2}}{2\Delta S_{vap}} - C \\ &= \frac{RB \pm \sqrt{(RB)^2 - 4C\Delta S_{vap}RB}}{2\Delta S_{vap}} - C \end{aligned}$$

We must choose the solution with the plus sign only. Since the expression in the square root may be either larger or smaller than RB, depending on the sign of C, taking the minus sign as a possible answer could result in getting a negative temperature. Thus we only except the plus sign as it will guarantee a physical solution. Therefore:

$$T = \frac{RB + \sqrt{(RB)^2 - 4C\Delta S_{vap}RB}}{2\Delta S_{vap}} - C \tag{6}$$

3

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$\begin{aligned} \Delta G_r &= G_{final} - G_{initial} \\ &= \sum_i n_i \mu_i - \sum_i n_i^0 \mu_i \\ &= \sum_i (n_i - n_i^0)\mu_i \end{aligned}$$

Meanwhile,

$$\begin{aligned} \xi &= \frac{n_i - n_i^0}{\nu_i} \\ n_i - n_i^0 &= \xi \nu_i \end{aligned}$$

So,

$$\begin{aligned} \Delta G_r &= \xi \sum_i \nu_i \mu_i \\ &= \xi(2\mu_{HI_{(g)}} - \mu_{H_{2(g)}} - \mu_{I_{2(g)}}) \end{aligned}$$

Since $\mu_A \approx \Delta G_f[A]/\text{mol}$ (ignoring ΔG_{mixing}), and μ for an element in its standard state is 0, this expression can be simplified:

$$\begin{aligned} \Delta G_r &= \xi(2\mu_{HI_{(g)}} - \mu_{I_{2(g)}}) \\ &\approx \xi(2\Delta G_f[HI_{(g)}] - \Delta G_f[I_{2(g)}]) \end{aligned}$$

Note: We don't actually have to ignore ΔG_{mixing}.

$$\begin{aligned}
\Delta G_{mixing} &= RT\sum_i n_i \ln x_i \\
&= RT\left[\left(n^0_{H_2}+\xi\nu_{H_2}\right)\ln\frac{n^0_{H_2}+\xi\nu_{H_2}}{n}+\left(n^0_{I_2}+\xi\nu_{I_2}\right)\ln\frac{n^0_{I_2}+\xi\nu_{I_2}}{n}\right. \\
&\quad \left.+\left(n^0_{HI}+\xi\nu_{HI}\right)\ln\frac{n^0_{HI}+\xi\nu_{HI}}{n}\right] \\
&= RT\left[(1-\xi)\ln\frac{1-\xi}{2}+(1-\xi)\ln\frac{1-\xi}{2}+(2\xi)\ln\frac{2\xi}{2}\right] \\
&= 2RT\left[(1-\xi)\ln\frac{1-\xi}{2}+\xi\ln\xi\right]
\end{aligned}$$

Then,

$$\Delta G_r = \xi(2\mu_{HI_{(g)}}-\mu_{I_{2(g)}})+2RT\left[(1-\xi)\ln\frac{1-\xi}{2}+\xi\ln\xi\right]$$

(b)

$$H_{2(g)}+I_{2(s)}\rightleftharpoons 2HI_{(g)}$$

$$\begin{aligned}
\Delta G_r &= \xi(2\mu_{HI_{(g)}}-\mu_{H_{2(g)}}-\mu_{I_{2(s)}}) \\
&= 2\xi\mu_{HI_{(g)}} \\
&\approx 2\xi\Delta G_f[HI_{(g)}]
\end{aligned}$$

Notice that if the reaction coefficients were halved, the reaction expression would represent the formation of $HI_{(g)}$ from its constituent elements in their standard states (*i.e.* the definition of the formation reaction for $HI_{(g)}$), and the 2 could be omitted from the above expression. Also, if $\xi = 1$ in (a) or (b), the equations involving ΔG_f become exact because $\Delta G_{mixing} = 0$.
Note: This time,

$$\Delta G_{mixing} = RT\left[(1-\xi)\ln\frac{1-\xi}{1+\xi}+2\xi\ln\frac{2\xi}{1+\xi}\right]$$

because $I_{2(s)}$ is not involved in mixing. n instead represents the total number of moles of gas:

$$n = (1-\xi)+2\xi = 1+\xi$$

4

(a) Pressure exerted is $Force/Area$:

$$\begin{aligned} P = F/A = mg/lw &= (70kg)(9.81N/kg)/(2.5x10^{-5}m)(7.5x10^{-2}m) \\ P &= 3.66x10^{8}Pa \end{aligned} \tag{7}$$

(b) Clapeyron Equation for phase coexisitence: $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$ with $\Delta S = \frac{\Delta H_{fus}}{T}$
So ,

$$\frac{dP}{dT} \approx \frac{\Delta P}{\Delta T} = \frac{\Delta H_{fus}}{T\Delta V} \tag{8}$$

$\Delta V = \rho_{liquid}^{-1} - \rho_{ice}^{-1} = -8.69x10^{-2}cm^3/g = -8.69x10^{-5}m^3/kg$ .... Negative!

$$\begin{aligned} \frac{\Delta P}{\Delta T} &= \frac{-(6.12kJmol^{-1})(1mol)}{(0.018kg)(273.16K)(8.69x10^{-5}m^3/kg)} \\ \frac{\Delta P}{\Delta T} &= -1.43x10^{7}PaK^{-1} \end{aligned} \tag{9}$$

Now, $\Delta P = P_{skate} - P(1atm) = 3.66x10^{8}Pa$, and $T_1 = 273.16K$
So, $T_2 = 247.6K$

5

In this problem we can consider two states. the first state is the reaction without catalyst at equilibrium, and the second state is the reaction with catalyst at equilibrium.

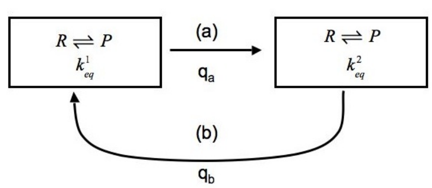

Figure 1: The 2 states represent the reaction R ⇔ P at 2 different equilibrium positions. The equilibrium position is determined by the presence or absence of a catalyst and the process by which one state is converted into another is the addition or removal of the catalyst. These processes involve heat flows as shown.

Consider separating these two processes so that we use process (a) as a hot reservoir, connect it to an engine with a cool reservoir and convert the heat into work. Subsequently we connect process (b) to the cool reservoir as a heat source for the process.

The situation in this figure is similar to what we saw in question 2. We have an engine that is performing work, however the net flow of heat is,

$$q_{net} = q_a - q_b + q_b = q_a \ .$$

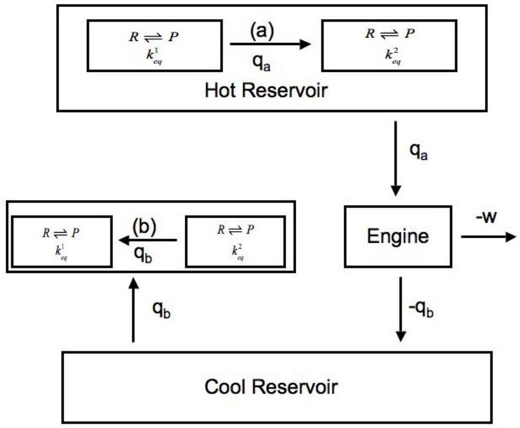

Figure 2: Composite engine. The Hot reservoir consists of the process of adding the catalyst to state 1. this process evolves heat which can flow into the heat engine. The engine is then connected to a cool reservoir in order to perform work without violating the second law of thermodynamics. The cool reservoir then acts as the heat source for process (b).

Thus heat from a single reservoir is being converted to work. This is a violation of Kelvin's principle.