Exam 1 solutions - Fall 2002

Question 1.) We have 100g of water in a beaker, and it is heated to 100 C by placeing it in contact with a temperature reservoir.

a.) Calculate the entropy change of the beaker of water.

The solution to this problem will depend on whether or not you considered if the water would boil. We didnt expect you to consider this but many people actually did.

$$Cp = 4.184 \cdot \frac{J}{K \cdot g} \qquad \Delta H_{evap} = 41 \cdot \frac{kJ}{mole} \qquad M_{water} = 18 \cdot \frac{g}{mole}$$

$$ds = \frac{\delta Q}{T} = 100 \cdot Cp \cdot \frac{dT}{T} \qquad \boxed{\Delta S_{water} = 100 \cdot Cp \cdot \ln\left(\frac{T_2}{T_1}\right)}$$

without boiling......

$$\Delta S_{water} := 100 \cdot 4.184 \cdot \ln\left(\frac{373}{293}\right) \qquad \boxed{\Delta S_{water} = 101.004} \quad \frac{J}{K}$$

with boiling......

$$\Delta S_{water} = 100 \cdot Cp \cdot \ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_{evap}}{T_{evap}} \qquad \Delta S_{water} := 100 \cdot 4.184 \cdot \ln\left(\frac{373}{293}\right) + \frac{41000}{373 \cdot 18} \cdot 100 \qquad \boxed{\Delta S_{water} = 711.668} \quad \frac{J}{K}$$

b.) What is the entropy change of the universe?? First, we shall find the entropy change of the reservoir....

Because the reservoir is at constant temperature, we know that $\boxed{\Delta S = \dfrac{Q_{res}}{T_{res}}}$ and we know that the heat that flowed into the beaker flowed out of the reservoir.

$$Q_{res} = -100 Cp \cdot (T_2 - T_1) \qquad Q_{res} := -100 \cdot 4.184 \cdot (100 - 20) \qquad \boxed{Q_{res} = -3.347 \times 10^4 \ J}$$

$$\Delta S_{res} := \frac{Q_{res}}{373} \qquad \boxed{\Delta S_{res} = -89.737} \quad \frac{J}{K}$$

if you included boiling.......

$$\Delta S_{res} = \frac{Q_{res}}{T_{res}} - \frac{\Delta H_{evap}}{T_{evap}} \qquad \Delta S_{res} := \frac{-3.347 \times 10^4}{373} - \frac{41000}{373 \cdot 18} \cdot 100 \qquad \boxed{\Delta S_{res} = -700.396} \quad \frac{J}{K}$$

now for the entropy change of the universe......

$$\Delta S_{univ} = \Delta S_{water} + \Delta S_{res}$$

without boiling......

$$\Delta S_{univ} := \frac{Q_{res}}{373} + 100 \cdot 4.184 \cdot \ln\left(\frac{373}{293}\right) \qquad \boxed{\Delta S_{univ} = 11.267} \quad \frac{J}{K}$$

with boiling.....

$$\Delta S_{univ} := \frac{Q_{res}}{373} - \frac{41000}{373 \cdot 18} \cdot 100 + 100 \cdot 4.184 \cdot \ln\left(\frac{373}{293}\right) + \frac{41000}{373 \cdot 18} \cdot 100 \qquad \boxed{\Delta S_{univ} = 11.267} \quad \frac{J}{K}$$

You notice that the entropy change of the universe is positive, as you would expect. Also, note that boiling has no effect on the total entropy change.

c.) A carnot engine gives reversible heat transfer, so the entropy change of the universe will be zero

2. $dU = TdS + V\cdot\sigma_{xx}\cdot d\varepsilon_{xx} + V\cdot\sigma_{yy}\cdot d\varepsilon_{yy} + V\cdot\sigma_{zz}\cdot d\varepsilon_{zz} + E\cdot dP$ Note: The pressure is absorbed into the stresses.

a.) We want a function of T, εxx, σyy, σzz, and E.

$\phi = U - TS - V\cdot\sigma_{yy}\cdot\varepsilon_{yy} - V\cdot\sigma_{zz}\cdot\varepsilon_{zz} - EP$ $d\phi = -SdT + V\cdot\sigma_{xx}\cdot d\varepsilon_{xx} - V\cdot\varepsilon_{yy}\cdot d\sigma_{yy} - V\cdot\varepsilon_{zz}\cdot d\sigma_{zz} - PdE$

b.) $-S = f1\left(T,\varepsilon_{xx},\sigma_{yy},\sigma_{zz},E\right)$

$V\cdot\sigma_{xx} = f2\left(T,\varepsilon_{xx},\sigma_{yy},\sigma_{zz},E\right)$

$-V\cdot\varepsilon_{yy} = f3\left(T,\varepsilon_{xx},\sigma_{yy},\sigma_{zz},E\right)$

$-V\cdot\varepsilon_{zz} = f4\left(T,\varepsilon_{xx},\sigma_{yy},\sigma_{zz},E\right)$

$-P = f5\left(T,\varepsilon_{xx},\sigma_{yy},\sigma_{zz},E\right)$

3. Start with the following expression......

$$dL = \left(\frac{\partial}{\partial\sigma}L\right)_T \cdot d\sigma + \left(\frac{\partial}{\partial T}L\right)_\sigma \cdot dT$$ we will use this to get $\frac{1}{L}\cdot\left(\frac{\partial}{\partial\sigma}L\right)_S$

$$\frac{1}{L}\cdot\left(\frac{\partial}{\partial\sigma}L\right)_S = \frac{1}{L}\cdot\left(\frac{\partial}{\partial\sigma}L\right)_T + \frac{1}{L}\cdot\left(\frac{\partial}{\partial T}L\right)_\sigma\cdot\left(\frac{\partial}{\partial\sigma}T\right)_S$$ We know all these terms except for the very last derivative

$$\frac{1}{L}\cdot\left(\frac{\partial}{\partial\sigma}L\right)_S = \frac{1}{E_s} \qquad \frac{1}{L}\cdot\left(\frac{\partial}{\partial\sigma}L\right)_T = \frac{1}{E_T} \qquad \frac{1}{L}\cdot\left(\frac{\partial}{\partial T}L\right)_\sigma = \alpha_L \qquad \left(\frac{\partial}{\partial\sigma}T\right)_S = \frac{-\left(\frac{\partial}{\partial\sigma}S\right)_T}{\left(\frac{\partial}{\partial T}S\right)_\sigma}$$

we can now write.......

$$\frac{1}{E_s} = \frac{1}{E_T} + \alpha_L\cdot\left[\frac{-\left(\frac{\partial}{\partial\sigma}S\right)_T}{\left(\frac{\partial}{\partial T}S\right)_\sigma}\right]$$

$$\left(\frac{\partial}{\partial\sigma}S\right)_T = A\cdot\left(\frac{\partial}{\partial T}L\right)_\sigma = A\cdot L\cdot\alpha_L$$

$$\left(\frac{\partial}{\partial T}S\right)_\sigma = \frac{C_\sigma}{T}$$

we found this using the maxwell relation of the following potential

$$d\phi = -SdT - A\cdot L\cdot d\sigma$$

substituting all this stuff in, we get.....

$$\boxed{\frac{1}{E_S} = \frac{1}{E_T} - \frac{\left(\alpha_L\right)^2\cdot T\cdot V}{C_\sigma}}$$ NOTE: This derivation is totally analogous to deriving Cp-Cv

Now we need to estimate the relative difference between the two.

$$\alpha L \sim 10^{-5}\cdot\frac{1}{K} \qquad \frac{C_\sigma}{V} \text{ is roughly the same as } \frac{C_P}{V} \qquad \frac{C_P}{V} = \frac{25\cdot J}{mol\cdot K}\cdot\frac{1\cdot mol}{60\cdot g}\cdot\frac{10g}{cc} = \frac{4.2\cdot J}{K\cdot cc} = \frac{4.2\cdot10^6\cdot J}{K\cdot m^3}$$

$$\frac{\left(\alpha_L\right)^2\cdot T\cdot V}{C_\sigma} = 7.1\cdot10^{-15}$$ if we assumed a temperature of 300K   so then

$$\frac{E_T - E_S}{E_T \cdot E_S} = -\frac{(\alpha_L)^2 \cdot T}{C_\sigma} \qquad \text{assume that } E_S \cdot E_T = <E>^2 \qquad \text{so then...} \qquad \frac{E_T - E_S}{<E>} = -\frac{(\alpha_L)^2 \cdot T}{C_\sigma} \cdot <E> = -7.1 \cdot 10^{-15} \cdot <E>$$

if <E> is roughly 100 GPa, then $\qquad \dfrac{E_T - E_S}{<E>} \sim \text{-1\%}$

4. We have a piston attached to a generator.....

    a.) what is the final temperature of the gas?

        denote the environment pressure by P_o

        work done by the gas: $-P \cdot dV$

        work done on environment: $P_o \cdot dV$

        work done on generator: $(P - P_o) \cdot dV$

We know that the work done on the generator is fed back into the gas as heat, so....

$dU_{gas} = C_V \cdot dT = (P - P_o) \cdot dV - P \cdot dV = -P_o \cdot dV$ we will solve this for the final temperature, and we know the final pressure is Po.

$$C_V \cdot (T_2 - T_1) = -P_o \cdot (V_2 - V_1) = -P_o \cdot \left(\frac{R \cdot T_2}{P_o} - \frac{R \cdot T_1}{P_1}\right) \qquad (C_V + R) \cdot T_2 = \left(\frac{P_o}{P_1} \cdot R + C_V\right) \cdot T_1$$

$$\boxed{T_2 = \left(\frac{\frac{R}{10} + C_V}{R + C_V}\right) \cdot T_1 = \frac{26}{35} \cdot T_1}$$

    b.) define the environment as everything except the piston/gas assembly and the generator. There was no heat flow to the environment so the entropy of the environment doesnt change.

    c.) No. the entropy of the system increases, so the total entropy change is greater than zero and therefore irreversible.

5. find the metastable melting point of ε.

    we want to know where $\Delta G_{\varepsilon - L}(T) = 0$

$$\Delta G_{\varepsilon - L} = \Delta G_{\varepsilon - \beta} + \Delta G_{\beta - L} = \Delta H_{\varepsilon - \beta} + \Delta H_{\beta - L} - T \cdot (\Delta S_{\varepsilon - \beta} + \Delta S_{\beta - L})$$

$$\Delta H_{\varepsilon - \beta} = T_{\varepsilon - \beta} \cdot \Delta S_{\varepsilon - \beta} \qquad \Delta H_{\beta - L} = T_{\beta - L} \cdot \Delta S_{\beta - L}$$

$$\boxed{T_M = \frac{\Delta H_{\varepsilon - \beta} + \Delta H_{\beta - L}}{\Delta S_{\varepsilon - \beta} + \Delta S_{\beta - L}} = 1735.6 \text{ Kelvin}}$$