

Exam 1 - Solutions
3.20 MIT
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Question 1 (SOLUTION)

I have a machine stirring in a bucket with liquid. The bucket is under constant pressure and is insulated from the environment (an adiabatic bucket).

a) Which of the following statements regarding the enthalpy of the bucket during this process is correct? The bucket is defined as the physical bucket + the liquid in it.

$H_{\text{bucket}} > 0$ X $H_{\text{bucket}} < 0$ _____ $H_{\text{bucket}} = 0$ _____

In general it is easy to derive that $(dH)_p = (Q)_p + (W')_p$ where W' are all the work terms that are not $-pdV$. Stirring is such a work term (a form of mechanical work). Hence since work is performed on the bucket $W' > 0$, hence $dH > 0$.

b) Which of the following statements regarding the entropy of the bucket during this process is correct? The bucket is defined as the physical bucket + the liquid in it.

$S_{\text{bucket}} > 0$ X $S_{\text{bucket}} < 0$ _____ $S_{\text{bucket}} = 0$ _____

The stirring is irreversible and the stirring work will be dissipated as heat. Hence S increases.

c) Which of the following statements regarding the enthalpy of the surroundings is correct?

$H_{\text{surr}} > 0$ _____ $H_{\text{surr}} < 0$ X $H_{\text{surr}} = 0$ _____

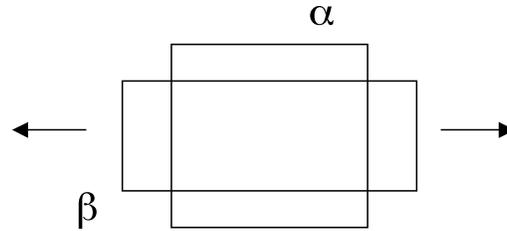
Same analysis as in part b, but now for the surroundings. It has to perform work, hence the enthalpy of the surroundings decreases.

d) What is the minimal entropy change that needs to place in the surroundings. ?

$S_{\text{surr}} > 0$ _____ $S_{\text{surr}} < 0$ _____ $S_{\text{surr}} = 0$ X

The minimal entropy change in the surroundings will take place when the work needed for the stirring is produced reversibly. In this case $S_{\text{surr}} = 0$.

Problem 2



(a)

$$dU = TdS + Fdl$$

We can define G as

$$G = U - TS - Fl \implies dG = -SdT - ldF$$

We now have a potential $G(T, F)$

(b)

Clapeyron-type equation

$$\frac{dF}{dT} = -\frac{\Delta S}{\Delta l} \implies \frac{d\sigma}{dT} = -\frac{\Delta H}{T\Delta\varepsilon V}$$

We can integrate and get

$$\Delta\sigma = -\frac{\Delta H}{\Delta\varepsilon V} \ln\left(\frac{T_2}{T_1}\right)$$

If we use the data from the problem

$$\frac{\Delta H}{\Delta\varepsilon V} = \frac{300 \frac{J}{mole}}{-0.07 \cdot 8 \times 10^{-6} \frac{m^3}{mole}} = 530 MPa$$

Now that we evaluated the constant term, we can find the upper and lower limits

Upper limit:

$$+70 MPa = 530 MPa * \ln\left(\frac{T_{upper}}{298 K}\right)$$

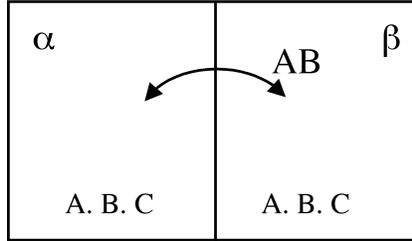
$$T_{upper} = 340 K$$

Lower limit:

$$-20 MPa = 530 MPa * \ln\left(\frac{T_{lower}}{298 K}\right)$$

$$T_{lower} = 287 K$$

Problem 3



First we need to find the potential that would be minimal under these conditions, namely G (constant T & P and flowing matter)

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

We are told temperature and pressure are constant, so those terms can be ignored. We now expand dG for each side of the system (called α and β here)

$$dG = dG^\alpha + dG^\beta$$

$$dG = \mu_A^\alpha dn_A^\alpha + \mu_B^\alpha dn_B^\alpha + \mu_A^\beta dn_A^\beta + \mu_B^\beta dn_B^\beta$$

Remember component C does not enter into the equilibrium because it cannot be moved. We now use information given in the problem to write everything in terms of dn_A^α , namely

$$dn_A^\alpha = -dn_A^\beta$$

$$dn_B^\alpha = -dn_B^\beta$$

$$dn_A^\alpha = dn_B^\alpha$$

So now we have

$$dG = \mu_A^\alpha dn_A^\alpha + \mu_B^\alpha dn_B^\alpha - \mu_A^\beta dn_A^\beta - \mu_B^\beta dn_B^\beta$$

$$dG = \left[\mu_A^\alpha + \mu_B^\alpha - (\mu_A^\beta + \mu_B^\beta) \right] dn_A^\alpha$$

For dG to be zero, the term in brackets must be zero

$$\mu_A^\alpha + \mu_B^\alpha - (\mu_A^\beta + \mu_B^\beta) = 0$$

$$\boxed{\mu_A^\alpha + \mu_B^\alpha = \mu_A^\beta + \mu_B^\beta}$$

Problem 4

For $S(T, V)$ start with the differential for S as a function of T and V

$$dS = \left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT$$

Now all we have to do is manipulate the two partial derivatives to get them in terms of things we know

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad \text{(Maxwell)}$$

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{-1}{\left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{-V\alpha_v}{-V\beta_T} = \frac{\alpha_v}{\beta_T}$$

and

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{c_v}{T}$$

Putting this all together we get

$$dS = \left(\frac{\alpha_v}{\beta_T}\right) dV + \left(\frac{c_v}{T}\right) dT$$

We approach $S(V, p)$ in the same manner

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial V}\right)_p dV + \left(\frac{\partial S}{\partial p}\right)_V dp \\ \left(\frac{\partial S}{\partial V}\right)_p &= \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p && \text{(Chain Rule)} \\ \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p &= \frac{c_p}{T} \cdot \frac{1}{V\alpha_v} \\ \left(\frac{\partial S}{\partial V}\right)_p &= \frac{c_p}{TV\alpha_v} \end{aligned}$$

and

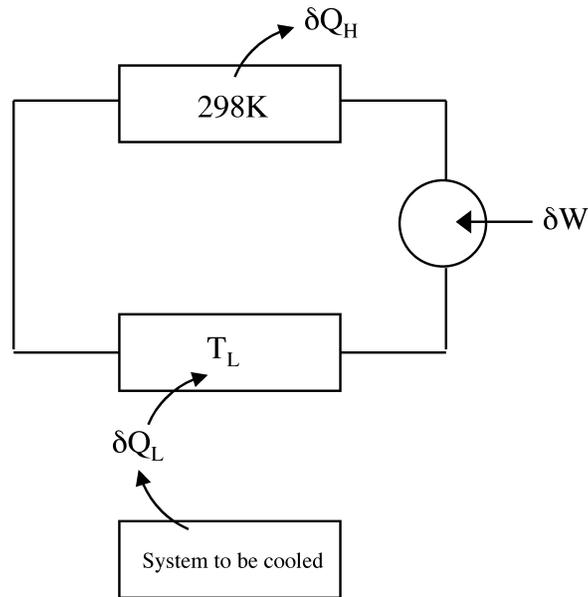
$$\begin{aligned} \left(\frac{\partial S}{\partial p}\right)_V &= \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial p}\right)_V && \text{(Chain Rule)} \\ \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial p}\right)_V &= \frac{c_v}{T} \cdot \frac{\beta_T}{\alpha_v} \end{aligned}$$

Putting all that together we get

$$dS = \left(\frac{c_p}{TV\alpha_v}\right) dV + \left(\frac{c_v\beta_T}{T\alpha_v}\right) dp$$

Note: There are other methods of getting at this answer, but they all involve starting with the differential form of dS with S as a function of the appropriate variables. The answers are equivalent if you remember the relationships between c_p and c_v and β_T and β_S .

Problem 5



We can use an ideal refrigerator. Starting with the first law,

$$\delta Q_L + \delta Q_H + \delta W = 0$$

and the second law

$$\frac{\delta Q_H}{T_H} + \frac{\delta Q_L}{T_L} = 0$$

$$\delta Q_H = -\frac{T_H}{T_L} \delta Q_L$$

Combining this with the first law

$$\delta Q_L \left(1 - \frac{T_H}{T_L}\right) + \delta W = 0$$

$$\delta W = \left(\frac{T_H}{T_L} - 1\right) \delta Q_L$$

But we can write δQ_L as

$$\delta Q_L = dH = -AdT > 0$$

(minus sign because heat is given to the heat reservoir at T_L and dT is negative)

$$\delta W = -A \left(\frac{T_H}{T} - 1\right) dT$$

$$W = \int_{298}^1 -A \left(\frac{T_H}{T} - 1\right) dT$$

$$W = \int_1^{298} A \left(\frac{T_H}{T} - 1\right) dT = [AT_H \ln T]_1^{298} - [AT]_1^{298} = AT_H \ln 298 - A(297)$$

$$W = 140 \text{ kJ}$$