ECHE 363 – Thermodynamics of Chemical Systems
Quiz 2

Name Solutions

100 points total.

Be sure to show all work to obtain maximum credit. Closed book and no notes.

Equations that may or may not be needed.

First Law for closed systems:

$$dU + dE_k + dE_p = \delta Q + \delta W$$

$$\Delta U + \Delta E_k + \Delta E_p = Q + W$$

PV work:

$$\delta w_m = -P_E dv_m$$

First Law for open systems with one input and one output stream:

$$\frac{dU}{dt} + \frac{dE_K}{dt} + \frac{dE_P}{dt} = \dot{n}_{in}\left[h_m + \frac{1}{2}|v|^2\,(MW) + gz(MW)\right]_{in} - \dot{n}_{out}\left[h_m + \frac{1}{2}|v|^2\,(MW) + gz(MW)\right]_{out} + \dot{Q} + \dot{W}_s$$

Differential entropy change for an ideal gas:

$$ds_m = c_{p,m}\frac{dT}{T} - R\frac{dP}{P}$$

Second Law for closed sstems:

$$\Delta S - \frac{Q}{T_{surr}} \geq 0$$

Second Law for open systems with one input and one output stream:

$$\frac{dS_{univ}}{dt} = \frac{dS}{dt} + s_{m,out}\dot{n}_{out} - s_{m,in}\dot{n}_{out} - \frac{\dot{Q}}{T_{surr}} \geq 0$$

Units and constants:

R = 8.314 J/(mol K)

g = 9.8 m/s^2

1 bar = 10^5 Pa = 10^5 kg/(m s^2)

1. (20 points) Assess the validity of the following statement:

   For a system whose state changes between two fixed states, (P_1, T_1) and (P_2, T_2), the change in molar entropy is: $\Delta s_m = c_{p,m} \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$

   Select one: (Always True) (Sometimes True) (Always False)

   Briefly explain your answer:

   True for ideal gas only if $C_{p,m}$ can be treated as a constant

2. (20 points) A closed system undergoes a process taking it between two fixed states, (P_1, T_1) and (P_2, T_2), first in a reversible manner and then in an irreversible manner.

   a. (10 points) For which case (reversible or irreversible) is the entropy change of the system greater? Why?

   Same in both cases. Entropy is a state function (path-independent):

   $\therefore \Delta S_{rev} = \Delta S_{irrev}$

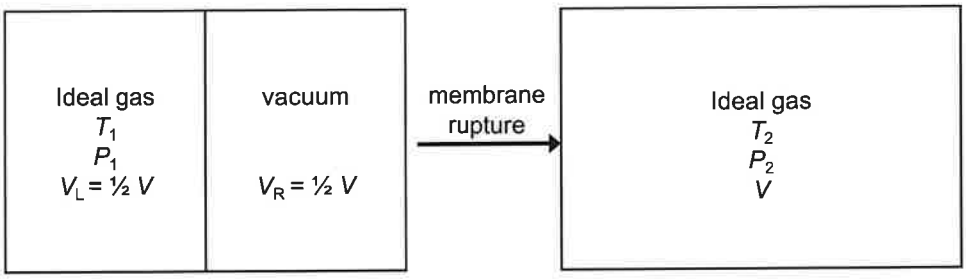
   b. (10 points) For which case (reversible or irreversible) is the entropy change of the universe greater? Why?

   2nd Law: $\Delta S_{univ} = \Delta S + \Delta S_{surr} \geq 0$

   $\Delta S_{univ,\,irrev} > \Delta S_{univ,\,rev}$

   $\Delta S_{univ} = 0$ is characteristic of a reversible process.

3. (60 points) A rigid insulated vessel with a total volume V (shown below) is separated by a membrane, such that the left (L) and right (R) chambers each comprise half the total volume of the vessel. The left chamber is initially filled with an ideal gas with at T_1, P_1. The right chamber is evacuated (vacuum). The membrane ruptures and the ideal gas fills the entire volume V.



a. (20 points) What are the final temperature T_2 and pressure P_2? Justify your answer using the First Law and any necessary property relations for an ideal gas. Express your answer in terms of T_1 and P_1.

1st Law: $\Delta U = \cancel{Q} + \cancel{W}$

$Q = 0$ (insulated); $W = 0$ (entire container is sys, $\Delta V = 0$)

$$\Delta U = 0 = \int_{T_1}^{T_2} C_{v,m}\, dT \Rightarrow \therefore \boxed{T_2 = T_1}$$

$$\frac{P_1 V_L}{R T_1} = \frac{P_2 V}{R T_2} \Rightarrow P_2 = P_1\left(\frac{V_L}{V}\right) \Rightarrow \boxed{P_2 = \frac{P_1}{2}}$$

b. (40 points) Derive an expression for the entropy change of the universe per mole of gas in the system for this process, $\Delta s_{m,\,univ}$.

$$\Delta S_{m,univ} = \Delta S_m + \Delta S_{m,surr}$$

$$\Delta S_{m,surr} = -\frac{Q}{T_{surr}} = 0 \quad \text{(adiabatic)}$$

$$\Delta S_m = \int_{T_1}^{T_2} \frac{C_{p,m}}{T}\, dT - \int_{P_1}^{P_2} \frac{R}{P}\, dP = -R \ln\left(\frac{1}{2}\right)$$

$\int_{T_1}^{T_2} \frac{C_{p,m}}{T}\, dT = 0$ $(T_1 = T_2)$

$$\Delta S_m = R \ln(2) \Rightarrow \boxed{\Delta S_{m,univ} = R \ln 2}$$