CHEMICAL ENGINEERING 141: THERMODYNAMICS

Fall 2020

MIDTERM – 120 MINUTES – 100 POINTS

Part I (20 pts): Conceptual questions (select **the only correct choice** from given choices)

1. The pressure of H_2O in a closed container is 1000 kPa and the temperature is 100 ˚C. The state of water phase is: B

a. Ideal gas b. Compressed liquid c. Superheated vapor
d. Saturated vapor e. Saturated liquid-vapor mixture

2. The specific enthalpy of atmospheric air most likely varies with: D

a. Its pressure b. Its volume c. Its density d. Its temperature

e. R (ideal gas constant)

3. An ideal gas is compressed in an isothermal process in a closed system. The process MUST also be: C

a. Adiabatic b. Isobaric c. Isenthalpic d. Isentropic e. Isochoric

4. For which type of process is the equation dQ = TdS always valid? C

a. Irreversible b. Isothermal c. Reversible d. Isobaric

5. The entropy of the universe is conserved: D

a. Never b. In an isothermal process c. Only if you have a cycle d. In a reversible process

6. When is the following equation always valid? E

$$\Delta U = \int_{T_1}^{T_2} CvdT$$

a. Isobaric path b. Isochoric path c. Ideal gas d. a and c e. b and c

7. An ideal gas is compressed to double its pressure in a piston along various reversible paths, and the final temperature remains the same as the initial temperature. Which of the following requires the most amount of work? A

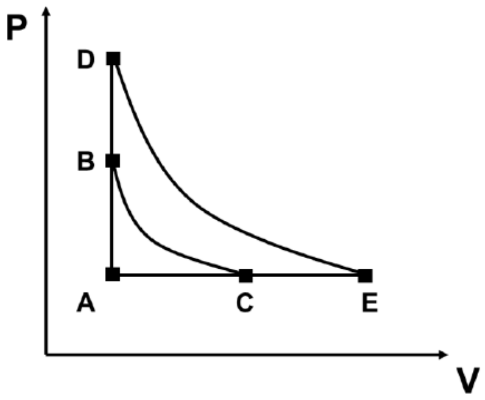
a. Isothermal compression

b. Isobaric compression followed by adiabatic compression

c. Isobaric compression followed by isochoric heating

d. All the same

8. Two reversible cycles are shown on a PV diagram. Which cycle has a larger value of Q? B



a. A→B→C→A

b. A→D→E→A

c. Q is the same for both processes

9. An idealized throttling process is: C

a. Isobaric b. Isothermal c. Isenthalpic d. b and c

10. Liquid water is used in a chemical reaction with other reactants. After the reaction, some of the liquid water becomes vapor. To calculate possible temperature change after the reaction, how many of the following heat effects may we have to consider? F

a. Sensible heat b. Latent heat c. Heat of reaction d. b and c

e. a and c f. a, b and c

Part II (80 pts): Show work and indicate your final answer clearly!

1. (20 pts) One mole of ideal gas with a temperature-independent heat capacity of c_p = 29.3 J/(mol K) undergoes the following cyclic sequence of quasi-static processes:

1. The gas is heated isobarically from 200 K and 2 bar until the temperature reaches 400 K.
2. The gas is adiabatically expanded until the temperature drops to 200 K.
3. The gas is isothermally compressed to its original pressure of 2 bar.

a. **(10 pts)** Calculate the heat, Q, work, W, change in internal energy, ΔU, and change in enthalpy, ΔH, for each step in the process.

b. **(5 pts)** Confirm that the changes in internal energy and enthalpy sum to zero for the cycle.

c. **(5 pts)** What are the net heat, Q, and net work, W, for this cycle?

Solution:

1 mole of gas, c_p = 29.3 J/mol K

For each step, we want Q, W, ΔU, and ΔH.

Step (1) Isobaric heating from 200K to 400K at 2 bar

For closed system with no change in kinetic or potential energy:

$$\Delta U = Q + W$$

$$Q = \Delta U - W = \Delta U + P\Delta V$$

$$\Delta \boldsymbol{H} = nc_p\Delta T = 1mol * \frac{29.3J}{mol\,K} * (400K - 200K) = \boldsymbol{5860J}$$

For isobaric heating, $\Delta H = \boldsymbol{Q} = \boldsymbol{5860J}$

$$\Delta \boldsymbol{U} = nCv\Delta T = 1mol * \left(\frac{29.3J}{mol\,K} - \frac{8.314J}{mol\,K}\right) * (400K - 200K) = \boldsymbol{4197J}$$

$$\boldsymbol{W} = \Delta U - Q = \boldsymbol{-1663J}$$

Step (2) Adiabatic expansion to T = 200K

$\boldsymbol{Q} = \boldsymbol{0\,J}$ by definition of adiabatic

$$\Delta \boldsymbol{U} = nCv\Delta T = 1mol * \left(\frac{29.3J}{molK} - \frac{8.314J}{molK}\right) * (200K - 400K) = \boldsymbol{-4197J}$$

$$\boldsymbol{W} = \Delta U - Q = \boldsymbol{-4197J}$$

$$\Delta \boldsymbol{H} = nCp\Delta T = 1mol * \frac{29.3J}{molK} * (200K - 400K) = \boldsymbol{-5860J}$$

Note that the pressure at the end of this step is:

$$P_2 = P_1 * \left(\frac{T_2}{T_1}\right)^{\frac{Cp}{R}} = 2bar * \left(\frac{200K}{400K}\right)^{3.5} = 0.177\ bar$$

Step (3) Isothermally compressed to 2 bar (T_1=T_2)

$$\Delta\boldsymbol{U} = nCv\Delta T = 0 = Q + W \;\; so \;\; Q = -W$$

$$\boldsymbol{W} = -\int_{V1}^{V2} PdV = -RT\int_{V1}^{V2}\frac{dV}{V} = -RTln\left(\frac{V2}{V1}\right) = RTln\left(\frac{P2}{P1}\right)$$
$$= 8.314 * 200 * \ln\left(\frac{2}{0.177}\right) = \mathbf{4032\,\boldsymbol{J}} = -Q \quad so \;\; \boldsymbol{Q} = -\mathbf{4032\,\boldsymbol{J}}$$

$$\Delta\boldsymbol{H} = nCp\Delta T = \mathbf{0\,\boldsymbol{J}}$$

Overall:

$$\Sigma\Delta U = (4197) + (-4197) + (0) = 0J$$
$$\Sigma\Delta H = (5860) + (-5860) + (0) = 0J$$
$$\Sigma Q = (5860) + (0) + (-4032) = 1828J$$
$$\Sigma W = (-1663) + (-4197) + (4032) = -1828J$$

2. (20 pts) You open the valve of a tank containing an ideal gas at 35 °C and 5.0 bar, so that the gas exits the tank into the atmosphere at 25 °C. The tank has a volume of 10 L, and the gas is being released from a tiny valve at a constant rate of 0.01 mol/h. How long until the air in the tank and the air in the environment are at the same temperature? Take c_V = 20.8 J/(mol K) for the air. Assume that there is no heat transfer between the tank and the surroundings.

Solution:

The open system, first law balance is:

$$\frac{d(mU)_{CV}}{dt} = Q + W - \Delta(H\dot{m})$$

You know that $Q = 0$ and $W = 0$. There is only one flow stream, so by a mass balance, $\dot{m} = -\frac{dm}{dt}$, where m is the mass of the contents of the tank.

Rewriting the first law balance and rearranging:

$$\frac{d(mU)_{CV}}{dt} = H\frac{dm}{dt}$$

$$d(mU)_{CV} = mdU + Udm = Hdm$$

$$mdU = (H - U)dm = PVdm$$

Now you can rearrange, substitute the Ideal Gas EOS, and integrate:

$$\frac{dm}{m} = \frac{dU}{PV} = \frac{C_V dT}{RT}$$

$$\int_{m_1}^{m_2} \frac{dm}{m} = \int_{T_1}^{T_2} \frac{C_V}{R}\left(\frac{dT}{T}\right)$$

$$\ln\left(\frac{m_2}{m_1}\right) = \frac{C_V}{R}\ln\left(\frac{T_2}{T_1}\right)$$

$$= \frac{20.8}{8.314}\ln\left(\frac{298}{308}\right) = -0.08258$$

$$\frac{m_2}{m_1} = 0.9207$$

So the tank needs to lose $1 - 0.9207 = 0.0793$ fraction of its contents. The number of moles in the tank currently is:

$$n = \frac{PV}{RT} = \frac{5.0 * 10.}{0.08314 * 308} = 1.95\, mol$$

$$1.95 * 0.0793 = 0.154$$

So the process will take $(0.154\, mol)/(0.01 \frac{mol}{h}) \ = \boxed{15.4\ h}$

3. **(20 pts)** With respect to 1 kg of liquid water (the heat capacity of liquid water is 4.2 J/(g K)):

a. **(10 pts)** Initially at 0˚C, it is heated to 80˚C by contact with a heat reservoir at 80˚C. What is the entropy change of the water? Of the heat reservoir? What is total entropy change?

b. **(5 pts)** Initially at 0˚C, it is first heated to 40˚C by contact with a heat reservoir at 40˚C and then to 80˚C by contact with a heat reservoir at 80˚C. What is total entropy change?

c. **(5 pts)** Explain how the water might be heated from 0˚C to 80˚C so that total entropy change is zero.

Solution:

Assume that the heat capacity of water is constant and equal to 4.184 kJ/kgK.

a) $T_1 = 273.15\ K$ and $T_2 = 353.15\ K$

$$Q = \ C_p(T_2 - T_1) = 336\ \frac{kJ}{kg\ K}$$

$$\Delta S_{H_2O} = C_p ln\frac{T_2}{T_1} = 1.079\ \frac{kJ}{kg\ K}$$

$$\Delta S_{res} = \frac{-Q}{T_{res}} = -0.951\ \frac{kJ}{kg\ K}$$

$$\Delta S_{tot} = \Delta S_{H_2O} + \Delta S_{res} = 0.128\ \frac{kJ}{kg\ K}$$

b) The entropy change of the water is the same as in part (a), and the total heat transfer is the same, but divided into two halves.

$$\Delta S_{res} = \frac{-Q}{2}\left(\frac{1}{313.15\ K} + \frac{1}{353.15\ K}\right) = -1.012\ \frac{kJ}{kg\ K}$$

$$\Delta S_{H_2O} = C_p ln\frac{T_2}{T_1} = 1.079\ \frac{kJ}{kg\ K}$$

$$\Delta S_{tot} = \Delta S_{H_2O} + \Delta S_{res} = 0.067\ \frac{kJ}{kg\ K}$$

c) The reversible heating of the water requires an infinite number of heat reservoirs covering the range of temperatures from 273.15 to 353.15 K, each one exchanging an infinitesimal quantity of heat with the water and raising its temperature by a differential increment.

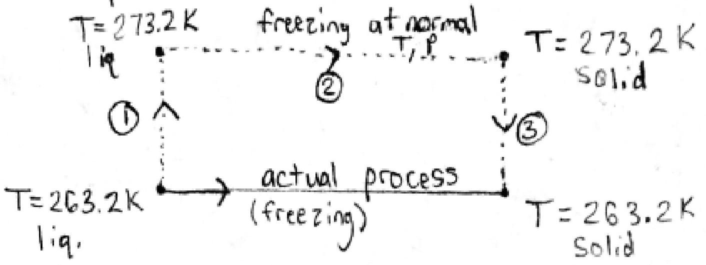
4. (20 pts) The normal melting temperature of water is 273.2K with a heat of fusion of ΔH^0=6012 J/mol.

a. **(10 pts)** Find the entropy change of one mole of water freezing at *T*=263.2K and normal pressure.

b. **(10 pts)** Find the total entropy change (system and surroundings) for this process. What does the sign of the result tell you about the process?

The heat capacities c_p of liquid and solid water are 75.6 J/(mol K) and 37.8 J/(mol K), respectively, and can be considered as constant.

a.) Since we only know ΔH°_{fus} at **273.2K**, we must construct hypothetical paths to find the entropy of the system.



* All steps are at P = 1 atm

* N = 1 mol

We can construct hypothetical paths with the same initial and final states because entropy is a state function.

$$\Delta S_{sys} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

Step 1: Isobaric heating of liq. H_2O from 263.2K to 273.2K

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \cancel{\left(\frac{\partial S}{\partial P}\right)_T dP}^{\text{const } P}$$

$$dS = \frac{N c_P}{T} dT$$

$$\xrightarrow{\text{integrate}} \Delta S_1 = N c_{P,liq} \ln\left(\frac{T_f}{T_i}\right) = (1\text{ mol})\left(75.6 \frac{J}{mol \cdot K}\right) \ln\left(\frac{273.2K}{263.2K}\right) = 2.82 \frac{J}{K}$$

Step 2: freezing at 273.2K

$$dS = \frac{\delta Q}{T} \overset{\text{const } P}{=} \frac{dH}{T}$$

* Phase transition at const T, P

$$\xrightarrow{\text{integrate}} \Delta S_2 = -\frac{N \Delta h^\circ_{fus}}{T} = -\frac{(1\text{ mol})(6012 \frac{J}{mol})}{273.2\text{ K}} = -22.01 \frac{J}{K}$$

step 3: cooling of solid H_2O from 273.2K to 263.2K

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \cancel{\left(\frac{\partial S}{\partial P}\right)_T dP}^{\text{const } P}$$

* Make sure to use solid heat capacity!

$$\rightarrow dS = \frac{N c_P}{T} dT \xrightarrow{\text{integrate}} \Delta S_3 = N c_{P,solid} \ln\left(\frac{T_f}{T_i}\right) = (1\text{mol})\left(37.8 \frac{J}{mol \cdot K}\right) \ln\left(\frac{263.2K}{273.2K}\right)$$

$$\rightarrow \Delta S_3 = -1.41 \frac{J}{K}$$

a.) (continued)

$$\Delta S_{system} = \Delta S_1 + \Delta S_2 + \Delta S_3$$
$$= (2.82 \tfrac{J}{K}) + (-22.01 \tfrac{J}{K}) + (-1.41 \tfrac{J}{K})$$
$$= \boxed{-20.6 \tfrac{J}{K} = \Delta S_{system}}$$

Check: answer should be negative because heat is lost as water goes from liq. to solid ✓

b.) $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$

* We need to find entropy change of the environment (ΔS_{surr}). Assume the environment acts as an isothermal temperature reservoir.

* Since the process occurs at constant pressure, we get:

$$dS = \frac{1}{T}[dU + PdV] = \frac{1}{T}[dH - PdV - VdP + PdV]$$

$$dS = \frac{dH}{T} - \frac{V}{T}\cancel{dP}^{\,0 \text{ (const P)}} = \frac{dH}{T}$$

$$\xrightarrow{\text{integrate}} \Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{system}}{T}$$ since heat lost by system is gained by surroundings

$\Delta H_{syst} = \Delta H_1 + \Delta H_2 + \Delta H_3$ (using same hypothetical paths)

$$\Delta H_1 = N c_{p,liq}(T_f - T_i) = (1\,mol)(75.6 \tfrac{J}{mol\cdot K})(273.2K - 263.2K) = 756\ J$$

$$\Delta H_2 = -\Delta H_{fus} = -(6012 \tfrac{J}{mol})(1\,mol) = -6012\ J$$

$$\Delta H_3 = N c_{p,solid}(T_f - T_i) = (1\,mol)(37.8 \tfrac{J}{mol\cdot K})(263.2K - 273.2K) = -378\ J$$

$$\rightarrow \Delta H_{sys} = (756\ J) + (-6012\ J) + (-378\ J) = -5634\ J$$

$$\rightarrow \Delta S_{surr} = -\frac{\Delta H_{sys}}{T} = \frac{-(-5634\ J)}{(263.2\ K)} = 21.4 \tfrac{J}{K}$$

$$\therefore \Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} = (-20.6 \tfrac{J}{K}) + (21.4 \tfrac{J}{K}) = \boxed{0.8 \tfrac{J}{K} = \Delta S_{tot}}$$

The positive sign of ΔS_{tot} indicates the process is spontaneous (i.e., irreversible).