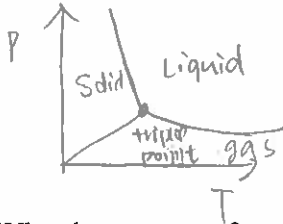


14

1. Short Answer. 3 points each

Note: questions are underlined - answer all questions.

(a) Sketch the P vs. T phase diagram for pure water, identifying solid, liquid, and gas phase regions. Show the two-phase boundaries and triple point.



(b) Why do we use reference conditions for thermodynamic data like U and H?

1) Energy is relative, not useful to study absolute energy

2) U, H are state variables. Path independent. choose good reference will make calculation easier

(c) For pure water (equilibrium conditions) at 1 atmosphere pressure and 90°C, can there be any vapor in the system? Why or why not?

Yes. There is vapor liquid equilibrium, so ~~some~~ some H₂O ~~can~~ escape liquid phase and stay as vapor (vapor pressure of H₂O)

(d) For ideal gases, liquids and solids, how does internal energy depend on pressure?

gas: ΔU not a function of P, no effect.

liquid/solid: ΔU not a function of P, no effect.

(e) Write the Gibbs phase rule, identifying the terms and give one example for a pure component (e.g. water).

$$DoF = 2 + C - \pi$$

C: # of components

π : # of phases

pure water, liq + vap phase

$$DoF = 2 + 1 - 2 = 1 \quad \text{--- need specifying temperature}$$

(f) At the liquid water - water vapor boundary in the presence of air (temperature T, pressure P), what is the mole fraction of air at the interface in terms of the water vapor pressure $P^*(T)$? What 'laws' are used for this analysis?

$$P_{H_2O} = P^*_{H_2O}(T) = y_{H_2O} \cdot P \quad P = x_{H_2O} \cdot P^*_{H_2O}(T)$$

$$y_{H_2O} = \frac{x_{H_2O} \cdot P^*_{H_2O}(T)}{P} = \frac{1 \cdot P^*(T)}{P}$$

$$y_{air} = 1 - y_{H_2O} = \boxed{1 - \frac{P^*(T)}{P}}$$

→ Raoult's law

(g) For a gas with 2 mole percent of some vapor component in contact with liquid water at 20°C and 3 atm, estimate the mole fraction of this component in water if the Henry's law coefficient is 6×10^4 atm/mole fraction.

Henry's:

$$P_A = y_A \cdot P_{tot} = x_A \cdot H_A(T)$$

$$y_A = 0.02$$

$$T = 20^\circ C \quad P = 3 \text{ atm}$$

$$x_A = \frac{y_A \cdot P_{tot}}{H_A(T)} = \frac{0.02 \times 3 \text{ atm}}{6 \times 10^4 \text{ atm/mole fraction}} = \boxed{1 \times 10^{-5} \text{ mole fraction}}$$

(h) Write the energy balance equations (assuming steady state) for a closed system and an open system, defining all terms. Include your assumptions regarding the sign conventions for heat and work.

closed: $\Delta U + \Delta E_k + \Delta E_p = Q - W$

internal energy → kinetic energy → potential energy
 heat → work

heat: into sys "+"
out sys. "-"

open: $\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} - \dot{W}_{shaft}$

enthalp → kinetic energy → potential energy → shaft work

work done by system "+"
done on sys. "-"

(i) What are the defining equations for heat capacity at constant volume and heat capacity at constant pressure?

$$C_v = \left(\frac{dU}{dt} \right)_v$$

$$C_p = \left(\frac{dH}{dt} \right)_p$$

(j) What does it mean to say the internal energy is a 'state variable'?

it's path-independent. only difference counts, doesn't matter where it starts.

XS

2. (30 Points)

Useful information:

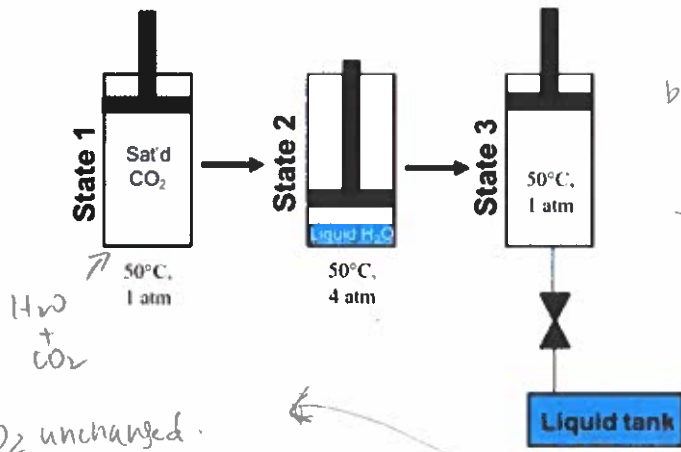
Antoine's Equation Parameters for water (P in mmHg, T in °C): A: 8.07131,

B: 1730.63, C: 233.426

Antoine's Equation: $\log(P^*) = A - B/(T+C)$

1 atm = 760 mmHg = 1.01325 bar

(a) [15 points] A cylinder is charged with water-saturated CO₂ at 50°C and 1 atm. The partial pressures are: $p_{CO_2} = 723.2$ mmHg, $p_{H_2O} = 36.8$ mmHg. The cylinder is compressed isothermally to 4 atm. A liquid take-out valve is opened and the liquid water is drained out. The cylinder is then returned to 50°C and 1 atm. What percentage of water vapor condenses in State 2?



State 1:

$$P_{CO_2} = y_{CO_2} \cdot P_{tot} \Rightarrow y_{CO_2} = 0.952$$

$$y_{H_2O} = 0.048$$

basis: 952 mol CO₂
→ 48 mol H₂O

State 2:

$$P_{H_2O}^*(50^\circ C) = 10$$

$$= 92.3 \text{ mmHg}$$

isothermally → Equilibrium

Raoult's law

$$P_{H_2O} = y_{H_2O} \cdot P_{tot} = x_{H_2O} \cdot P_{H_2O}^*$$

$$y_{H_2O} = \frac{x_{H_2O} \cdot P_{H_2O}^*}{P_{tot}} = \frac{1 \cdot 92.3 \text{ mmHg}}{760 \text{ mmHg} \times 4} = 0.0303$$

CO₂ unchanged.
CO₂ = basis
 $n_{tot} (1 - 0.0303) = 952 \text{ mol}$
 $n_{tot} = 981.8 \text{ mol}$
 $n_{H_2O, vapor} = 29.8 \text{ mol}$

$$\% \text{ condense} = \frac{48 - 29.8}{48} \times 100\% = 37.9\%$$

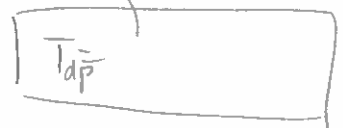
(b) [5 points] What is the dew point temperature in State 3?

State 3: $y_{CO_2} = 0.9697$
 $y_{H_2O} = 0.0303$

$$P_{H_2O} = 0.0303 \cdot 1 \text{ atm} = 0.0303 \text{ atm} = 23.028 \text{ mmHg} = P_{H_2O}^* (\text{dew point})$$

$$\log_{10}(23.028) = 8.07131 - \frac{1730.63}{233.426 + T_{dp}}$$

Solve for T_{dp} to get the solution



X9

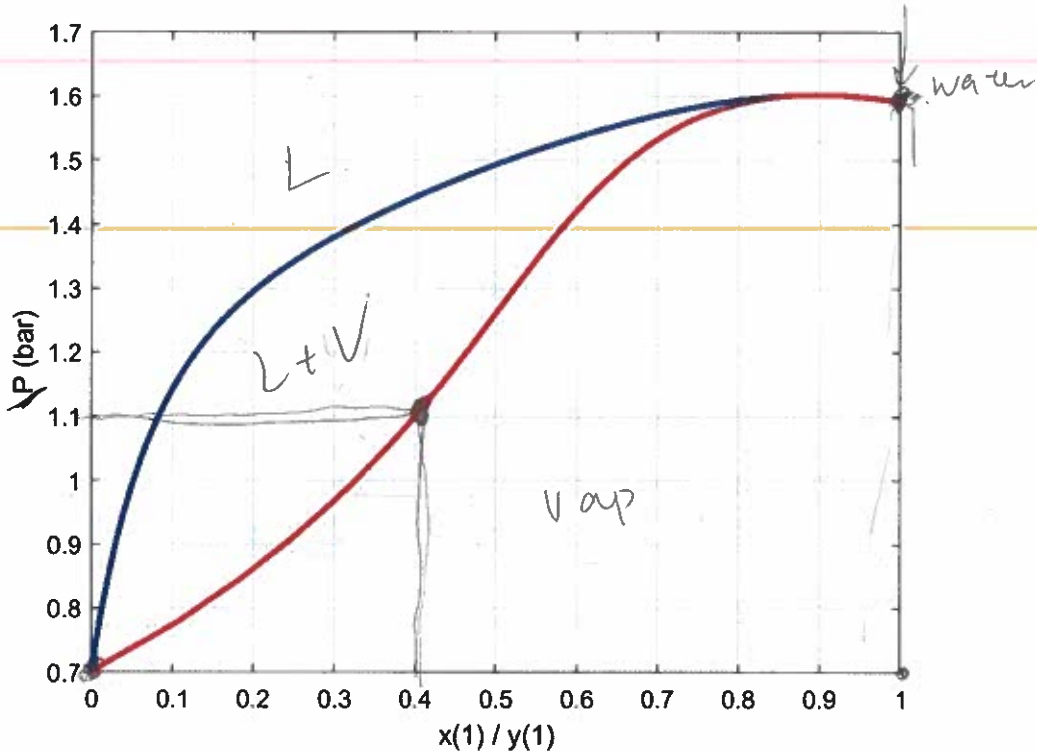
Useful information:

Antoine's Equation Parameters for water (P in mmHg, T in °C): A: 8.07131,

B: 1730.63, C: 233.426

Antoine's Equation: $\log(P^*) = A - B/(T+C)$

1 atm = 760 mmHg = 1.01325 bar



(c) [5 points] The diagram above describes the pressure versus composition of an ethanol/water mixture at 90°C. It is unknown which component is which (whether component 1 is ethanol or water). Find out what component 1 is and show the calculations you used to decide this. (No credit will be given for guesses without any work).

100% x₁ 90°C $P_{\text{eth}}^* (\text{gig}) = 10$ antw eq
 compare result with diagram

(d) [5 points] You have an ethanol/water mixture at a pressure of 1.1 bar and a composition of 0.4 (for component 1). How many degrees of freedom are there with this system?

$DOF = 2 + C - \pi$
 $= 2 + 2 - 2$
 $= 2$

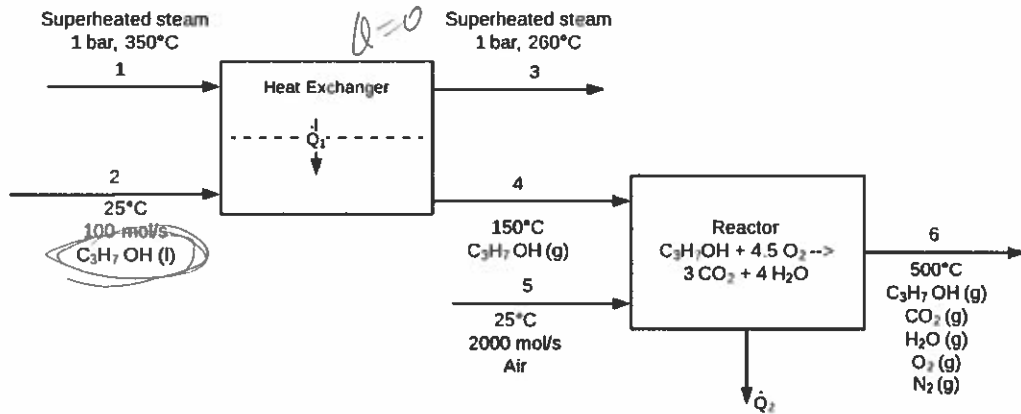
$2 \begin{cases} \nearrow x_1 \\ \searrow y_1 \end{cases}$

$5 \Rightarrow \boxed{0 \text{ dof overall}}$

49

3. (40 Points)

Consider the flow diagram below:



(a) [15 points] Solve for the heat transferred to stream 4 (Q_1) and the flowrate of steam in stream 1. The heat exchanger is adiabatic. Liquid n-propyl alcohol (C_3H_7OH) has a heat capacity of $150 \text{ J/mol } ^\circ\text{C}$, and gaseous C_3H_7OH has a heat capacity of $80 \text{ J/mol } ^\circ\text{C}$. C_3H_7OH boils at 97°C . The heat of vaporization C_3H_7OH is 50 kJ/mol . Steam tables are included below.

Table B.7 Properties of Superheated Steam*

P (bar) (T_{sat} , $^\circ\text{C}$)	Sat'd Water	Sat'd Steam	Temperature ($^\circ\text{C}$)							
			50	75	100	150	200	250	300	350
0.0	\hat{H} —	—	2595	2642	2689	2784	2880	2978	3077	3177
(-)	\hat{U} —	—	2446	2481	2517	2589	2662	2736	2812	2890
	\hat{V} —	—	—	—	—	—	—	—	—	—
0.1	\hat{H} 191.8	2584.8	2593	2640	2688	2783	2880	2977	3077	3177
(45.8)	\hat{U} 191.8	2438.0	2444	2480	2516	2588	2661	2736	2812	2890
	\hat{V} 0.00101	14.7	14.8	16.0	17.2	19.5	21.8	24.2	26.5	28.7
0.5	\hat{H} 340.6	2646.0	209.3	313.9	2683	2780	2878	2979	3076	3177
(81.3)	\hat{U} 340.6	2484.0	209.2	313.9	2512	2586	2660	2735	2811	2889
	\hat{V} 0.00103	3.24	0.00101	0.00103	3.41	3.89	4.35	4.83	5.29	5.75
1.0	\hat{H} 417.5	2675.4	209.3	314.0	2676	2776	2875	2975	3074	3176
(99.6)	\hat{U} 417.5	2506.1	209.2	313.9	2507	2583	2658	2734	2811	2889
	\hat{V} 0.00104	1.69	0.00101	0.00103	1.69	1.94	2.17	2.40	2.64	2.87
5.0	\hat{H} 640.1	2747.5	209.7	314.3	419.4	632.2	2855	2961	3065	3168
(151.8)	\hat{U} 639.6	2560.2	209.2	313.8	418.8	631.6	2643	2724	2803	2883
	\hat{V} 0.00109	0.375	0.00101	0.00103	0.00104	0.00109	0.425	0.474	0.522	0.571

*Adapted from R. W. Haywood, *Thermodynamic Tables in SI (Metric) Units*, Cambridge University Press, London, 1968. Water is a liquid in the enclosed region between 50°C and 350°C . \hat{H} = specific enthalpy (kJ/kg), \hat{U} = specific internal energy (kJ/kg), \hat{V} = specific volume (m^3/kg). Note: $\text{kJ/kg} \times 0.4303 = \text{Btu/lb}_m$.

1) bilan
 $\Delta \hat{H} + \Delta \hat{Q} + \Delta \hat{E}_p = 0$ adiabatic
 $\Rightarrow \Delta \hat{H}_{tot} = 0$

$\Delta \hat{H}_{tot} = \Delta \hat{H}_1 + \Delta \hat{H}_2 + \Delta \hat{H}_3 = 6504 \text{ kJ/s}$
 $\hat{Q}_1 = \Delta \hat{H}_{C_3H_7OH} = 6504 \text{ kJ/s}$
 $\Delta \hat{H}_{tot} = 0$

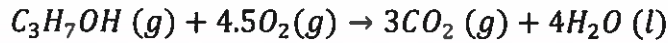
2) energy needed
 $25^\circ\text{C (l)} \xrightarrow{\Delta \hat{H}_1} 97^\circ\text{C (l)} \xrightarrow{\Delta \hat{H}_2} 97^\circ\text{C (g)} \xrightarrow{\Delta \hat{H}_3} 150^\circ\text{C (g)}$

$\Delta \hat{H}_{C_3H_7OH} + \Delta \hat{H}_{gas} = 0$
 $\Delta \hat{H}_{gas} = -6504 \text{ kJ/s}$

$\Delta \hat{H}_1 = 100 \frac{\text{mol}}{\text{s}} \cdot 150 \frac{\text{J}}{\text{mol} \cdot ^\circ\text{C}} \cdot (97 - 25)^\circ\text{C}$
 $\Delta \hat{H}_2 = 100 \frac{\text{mol}}{\text{s}} \times 50 \times 10^3 \frac{\text{J}}{\text{mol}}$
 $\Delta \hat{H}_3 = 100 \frac{\text{mol}}{\text{s}} \times 80 \frac{\text{J}}{\text{mol} \cdot ^\circ\text{C}} \times (150 - 97)^\circ\text{C} =$

$\Delta \hat{H} = \dot{m}(\hat{H}_{out} - \hat{H}_{in}) = -6504 \frac{\text{kJ}}{\text{s}}$
 $\hat{H}_{260} = 2975 + 0.2(3074 - 2975) = 2994.8$
 $\dot{m}_{steam} = \frac{6504 \text{ kJ/s}}{(2994.8 - 3176) \frac{\text{kJ}}{\text{kg}}} = 3589.4 \text{ kg/s}$

(b) [20 points] If conversion is 80% what is composition and molar flowrate of stream 6? How much heat must be removed from the reactor (\dot{Q}_2)? The specific standard heat of reaction (ΔH_r°) is -1000 kJ/mol. The heat of vaporization of water is 60 kJ/mol. Heat capacities are included below.



	C ₃ H ₇ OH (l)	C ₃ H ₇ OH (g)	O ₂ (g)	N ₂ (g)	H ₂ O (l)	H ₂ O (g)	CO ₂ (g)
C _p (J/mol °C)	150	80	30	25	100	36	50

~~$\Delta \hat{H} = \sum \dot{n}_i \hat{H}_i - \sum \dot{n}_j \hat{H}_j$~~ $\Rightarrow -\Delta \hat{H}_{tot} = \dot{Q}$

	\dot{n}_{in}	$\hat{H}_{ent.}$	\dot{n}_{out}	$\hat{H}_{ex.}$
C ₃ H ₇ OH (g)				
O ₂				
C ₃ H ₇ OH (l)				
CO ₂ (g)				
H ₂ O				
N ₂				

1) Cool rxn to 25°C

$$\Delta H_1 = -6504 \frac{kJ}{s}$$

2) heat from reaction

$$\Delta H_2 = 100 \frac{mol}{s} \cdot \frac{-1000 kJ}{mol}$$

$$\Delta H_3 = -10^5 \frac{kJ}{mol}$$

3) heat products to 500°C

80% conversion; product stream:

$$\dot{n}_{C_3H_7OH} = 20 \text{ mol/s}$$

$$\dot{n}_{CO_2} = 80 \cdot 3 = 240 \text{ mol/s}$$

$$\dot{n}_{H_2O} = 4 \cdot 80 = 320 \text{ mol/s}$$

$$\dot{n}_{O_2} = 2000 \cdot (0.21) \cdot (0.5) \cdot (0.2) = 378 \text{ mol/s}$$

$$\dot{n}_{N_2} = 1580 \text{ mol/s}$$

$\dot{Q} = \Delta H_{tot} = \Delta H_1 + \Delta H_2 + \Delta H_3$

$$\dot{Q} = \frac{20 \cdot 10^5}{1} = 80$$

\Rightarrow next calculate

$$\dot{H}_3 = \sum \dot{n}_i \int_{25^\circ C}^{500^\circ C} C_{pi}$$

C_{pi} in table.
n_i calculated

(c) **EXTRA CREDIT:** (5 points) The vapor leaving the reactor is fed to a turbine and leaves the turbine with an outlet temperature of 110°C. How much work you can produce?

