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Chemical Engineering 141: Thermodynamics

Spring 2014

Monday, April 7th, 2014

Midterm 1 – 50 minutes – 100 points total

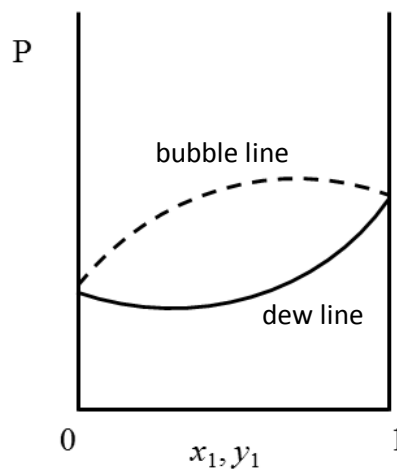
Turn in equation sheet with exam

Part I: Concept Questions

1. (1 point) For the same compression ratio, the Diesel engine has a higher efficiency than the Otto engine. (T/F)

_____ False _____

2. (1 point) Label the bubble line (saturated liquid) and the dew line (saturated vapor) on the figure below.



3. (1 point) Please describe the physical meaning of a residual property in one sentence or less.

Residual properties represent deviation from ideality.

4. (1 point) Large heat-transfer surfaces are important for steam power plants and internal-combustion engines (T/F).

_____ False _____

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5. (2 points) The Rankine cycle differs from the Carnot cycle in all but which of the following ways (circle one)?
- (a) The heating step is carried well beyond vaporization so as to produce a superheated vapor.
 - (b) The cooling step brings about complete condensation, yielding saturated liquid.
 - (c) Power plants can be built to deviate from the cycle solely because of the irreversibilities of the work-producing and work-requiring steps.
 - (d) The cycle is completely reversible.**
6. (2 points) The Rankine cycle accounts for practical difficulties in the operation of which of the following sets of equipment in a steam power plant (choose one)?
- (a) Turbines and compressors
 - (b) Pumps and turbines**
 - (c) Compressors and pumps
 - (d) Throttle valves and compressors
7. (2 points) Circle the required assumptions to reduce VLE calculations to Raoult's law:
- (a) Vapor phase is an ideal gas**
 - (b) Liquid phase is an ideal solution**
8. (2 points) The following methods may be used to calculate residual properties (circle one).
- (a) Virial equation
 - (b) Van der Waals
 - (c) Lee/Kesler
 - (d) All of the above**
9. (2 points) Circle the required assumptions to reduce VLE calculations to Henry's law:
- (a) Vapor phase is an ideal gas**
 - (b) Liquid phase is an ideal solution**
 - (c) Dilute solute in liquid phase**
10. (2 points) Circle the required assumptions to reduce VLE calculations to Modified Raoult's law:
- (a) Vapor phase is an ideal gas**
11. (1 point) An idealized throttle is:
- (a) Isenthalpic
 - (b) Isobaric
 - (c) Adiabatic
 - (d) A&B

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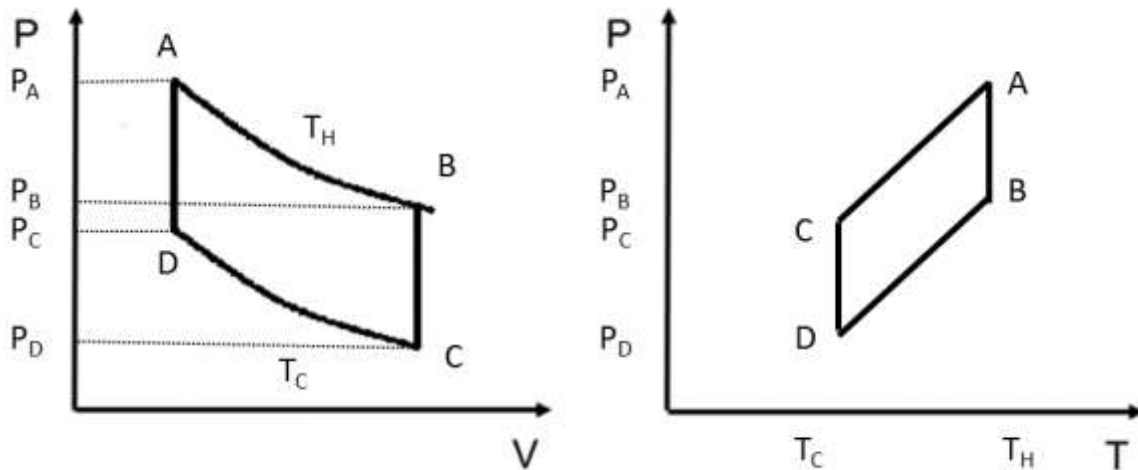
(e) A&C

An idealized throttle is: E: Isenthalpic and adiabatic. An idealized throttle only induces a pressure drop with no change in kinetic energy or potential energy with no heat transfer or shaft work done. This reduces the energy balance to $\Delta H=0$, therefore it is isenthalpic, but only if it is adiabatic.

12. (4 points) Consider a hypothetical engine (the idealized Stirling engine) composed of four steps:

- (i) Isothermal expansion
- (ii) Isochoric cooling
- (iii) Isothermal compression
- (iv) Isochoric heating

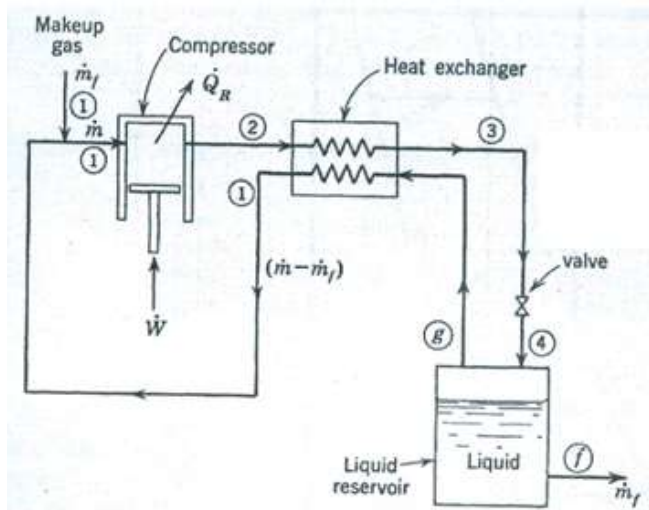
Draw a PV diagram and a PT diagram to represent the Stirling engine.



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13. (1 point) A schematic for the Linde process is shown below:



This process is an example of what type of process: liquefaction

14. (2 points) The Linde process relies on which of the following conditions to be met:

(a) $\mu = \left(\frac{\partial T}{\partial P}\right)_H > 0$

(b) $\mu = \left(\frac{\partial T}{\partial P}\right)_H < 0$ the gas must cool as it expands to condense.

(c) $\mu = \left(\frac{\partial T}{\partial P}\right)_H = 0$

15. (1 point) The coefficient μ is called: Joule-Thompson coefficient

Part II

16. (25 points) 3 mol of liquid A and 2 mol of liquid B are poured together into a container. The container is closed and the system is allowed to come to equilibrium. The pressure of the system at equilibrium is P . Assume you know P^{sat} for A and B.

Write out Raoult's law for both components. What assumptions are you making?

$$y_A P = x_A P_A^{sat}$$

$$y_B P = x_B P_B^{sat}$$

Assumptions: 1) vapor phase is an ideal gas, 2) liquid phase is an ideal solution or A and B are chemically similar

Set up a system of equations to solve for the total number of moles in the liquid phase, N_l . Clearly write and put a box around all equations in your system. Reduce the system to two equations with two unknowns. Write these final two equations in the space provided at the bottom of this page. Briefly explain how to find N_l without actually solving for it.

Note: use the variables N_v to represent the number of moles in the vapor phase and N_l to represent the number of moles in the liquid phase.

$$\begin{aligned} 3 \text{ mol A} &= N_l x_A + N_v y_A \\ 2 \text{ mol B} &= N_l x_B + N_v y_B \\ N_T = N_l + N_v &= N_A + N_B = 5 \\ x_A + x_B &= 1 \\ y_A + y_B &= 1 \\ y_A P &= x_A P_A^{sat} \\ y_B P &= x_B P_B^{sat} \end{aligned}$$

$$N_v = 5 - N_l \quad y_A = \frac{x_A P_A^{sat}}{P}$$

$$x_B = 1 - x_A$$

$$y_B = 1 - y_A = 1 - \frac{x_A P_A^{sat}}{P}$$

Solve for x_A in terms of N_l , then substitute into the other equation and solve for N_l .

$$\begin{aligned} 3 &= N_l x_A + (5 - N_l) \frac{x_A P_A^{sat}}{P} \\ 2 &= N_l (1 - x_A) + (5 - N_l) \left(1 - \frac{x_A P_A^{sat}}{P} \right) \end{aligned}$$

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Reduced equations using other variables (x_B, y_A, y_B):

$$2 = N_l x_B + (5 - N_l) \frac{x_B P_B^{sat}}{P}$$
$$3 = N_l (1 - x_B) + (5 - N_l) \left(1 - \frac{x_B P_B^{sat}}{P} \right)$$

$$3 = N_l \frac{y_A P}{P_A^{sat}} + (5 - N_l) y_A$$
$$2 = N_l \left(1 - \frac{y_A P}{P_A^{sat}} \right) + (5 - N_l) (1 - y_A)$$

$$2 = N_l \frac{y_B P}{P_B^{sat}} + (5 - N_l) y_B$$
$$3 = N_l \left(1 - \frac{y_B P}{P_B^{sat}} \right) + (5 - N_l) (1 - y_B)$$

17. (25 points) A phase change from liquid to vapor occurs at constant temperature and pressure.

- 1) Starting from fundamental property relations, please derive the Clapeyron equation, given below, for this phase change.

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\Delta V^{lv}}$$

- 2) The Clapeyron equation for vaporization may be simplified by introduction of reasonable approximations to the Clausius/Clapeyron equation. Please state TWO necessary assumptions and simplify the Clapeyron equation to the Clausius/Clapeyron equation, provided below.

$$\frac{d \ln P^{sat}}{d(1/T)} = - \frac{\Delta H^{lv}}{R}$$

PART 1

At equilibrium, the Gibbs free energies of the two phases must be equal

$$G^l = G^v$$

$$dG^l = dG^v$$

Substituting the fundamental Gibbs property relation for dG

$$V^l dP^{sat} - S^l dT = V^v dP^{sat} - S^v dT$$

which upon rearrangement becomes:

$$\frac{dP^{sat}}{dT} = \frac{S^v - S^l}{V^v - V^l} = \frac{\Delta S^{lv}}{\Delta V^{lv}}$$

The entropy change ΔS^{lv} and the volume change ΔV^{lv} are changes which occur when a unit amount of a pure chemical species is transferred from the liquid phase to the vapor phase at the equilibrium temperature and pressure. Integration of the fundamental enthalpy property relation yields the latent heat of phase transition:

$$dH = T dS + V dP = T dS \text{ (for const. } P\text{)}$$

$$\Delta H^{lv} = T \Delta S^{lv}$$

$$\Delta S^{lv} = \frac{\Delta H^{lv}}{T}$$

Substitution into our previous expression yields our solution:

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$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\Delta V^{lv}}$$

PART 2

The required assumptions are: (1) the vapor phase is an ideal gas and (2) the molar volume of the liquid is negligible compared with the molar volume of the vapor

The assumptions made are expressed by:

$$\Delta V^{lv} = V^v = \frac{RT}{P^{sat}}$$

Substitute to simplify the Clapeyron equation:

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\Delta V^{lv}} = \frac{\Delta H^{lv}}{TV^v}$$

$$\frac{dP^{sat}}{dT} = \frac{P^{sat}\Delta H^{lv}}{RT^2}$$

Separating T and P^{sat}

$$\frac{dP^{sat}}{P^{sat}} = \frac{\Delta H^{lv}}{R} \frac{dT}{T^2}$$

Taking T and P^{sat} inside the derivatives

$$d \ln P^{sat} = - \frac{\Delta H^{lv}}{R} d(1/T)$$

$$\frac{d \ln P^{sat}}{d(1/T)} = - \frac{\Delta H^{lv}}{R}$$

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18. (25 points) A hypothetical fluid (Oskium) is expanded through a turbine from an initial pressure and temperature of 100 kPa and 200°C, respectively to a final pressure of 20 kPa. Using the provided data for Oskium, find:

- 1) The work produced for an ideal turbine.
- 2) The entropy of the exit stream for a turbine efficiency of $\eta = 0.85$.

Superheated Oskium

P(kPa)	T(°C)	150	200	250	300	350	400	450	500
100	V	1	6	8	10	11	13	14	15
	U	5	8	9	10	11	12	13	14
	H	6	7	11	12	13	14	15	16
	S	6	7	8.5	9	9.5	10	10.5	11
200	V		2	4	6	7	9	10	11
	U	1	4	5	6	7	8	9	10
	H	2	6	7	8	9	10	11	12
	S	3	4	5	6	7	9	10	12

Saturated Oskium

P(kPa)	T(°C)	S(sat liq) kJ/kgK	S(sat vap) kJ/kgK	H(sat liq) kJ/kg	H(sat vap) kJ/kg	U(sat liq) kJ/kg	U(sat vap) kJ/kg	V(sat liq) m ³ /kg	V(sat vap) m ³ /kg
10	23	0.25	9	0.25	3	18	240	1	8000
15	34	0.50	8.75	0.50	3.5	19	242	1	7000
20	41	0.75	8.50	0.75	4	20	244	1	6000
25	48	1.00	8.25	1	4.5	21	246	1	5000
50	57	1.25	8	1.25	5	22	248	1	4000
100	63	1.50	7.75	1.50	5.5	23	250	1	3000
150	71	1.75	15	1.4	6	0.9	4.0	14	22

Solution:

a) From P₁, T₁, we can find H₁, S₁:

$$H_1 = 7 \text{ kJ/kg}$$

$$S_1 = 7 \text{ kJ/kg}$$

For an ideal turbine $S_1 = S_2 = 7 \text{ kJ/kgK}$

The final state is therefore P₂ = 20 kPa, S₂ = 7 kJ/kgK

$$S_2 = (x_{\text{vap}}) \cdot S_{\text{vap}} + (1 - x_{\text{vap}}) \cdot S_{\text{liq}}$$

$$7 = x_{\text{vap}} \cdot 8.5 + (1 - x_{\text{vap}}) \cdot 0.75 \Rightarrow x_{\text{vap}} = 0.806$$

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$$H_2 = x_{\text{vap}} H_{\text{vap}} + (1 - x_{\text{vap}}) H_{\text{liq}} = 0.806(4) + 0.194(0.75) = 3.37 \text{ kJ/kg}$$

$$\dot{W} = H_2 - H_1 = 3.63 \text{ kJ/kg}$$

$$\text{b) } \eta = 0.85 = (H_2 - H_1) / (H_2' - H_1) = (H_2 - 7) / (3.37 - 7)$$

$$H_2 = 3.91 \text{ kJ/kg}$$

Now have H_2 , P_2 specifies S_2

$$H_2 = x_{\text{vap}} H_{\text{vap}} + (1 - x_{\text{vap}}) H_{\text{liq}}$$

$$3.91 \text{ kJ/kg} = x_{\text{vap}}(4) + (1 - x_{\text{vap}})(0.75)$$

$$x_{\text{vap}} = 0.97$$

$$S_2 = x_{\text{vap}} S_{\text{vap}} + (1 - x_{\text{vap}}) S_{\text{liq}} = 0.96(8.5) + 0.04(0.75) = 8.27 \text{ kJ/kg K}$$