

Name \_\_\_\_\_

Wednesday, April 17<sup>th</sup>

**ECHE 363 – Thermodynamics of Chemical Systems**  
**Midterm #2**

Rules:

- 75 minutes total time. Once time is up, put aside answer sheets.
- Be sure to show all work to obtain maximum credit. This includes showing and simplifying any mass/mole, 1<sup>st</sup> Law, and 2<sup>nd</sup> Law balances that are needed to solve each problem.
- Closed book and no notes.
- Write your name on every page.
- Please only write on the front side of each page. Ask for additional paper if necessary.

Name \_\_\_\_\_

For instructor use only:

Problem 1 / 35	
Problem 2 / 35	
Problem 3 / 30	
Total / 100 points	

Name \_\_\_\_\_

1. (35 points) You are designing a process in which a pure gas at  $P_1, T_1$  is fed to a steady-state adiabatic turbine at molar flow rate  $\dot{n}_{\text{in}}$ . The turbine exit stream is vapor at  $P_2, T_2$ . The properties of this real gas are well-described by the van der Duval equation of state:

$$P = \frac{1}{v_m - b} \left( RT - \frac{aP}{\sqrt{T}} \right)$$

where  $a$  and  $b$  are known constants, and  $b < v_m$ .

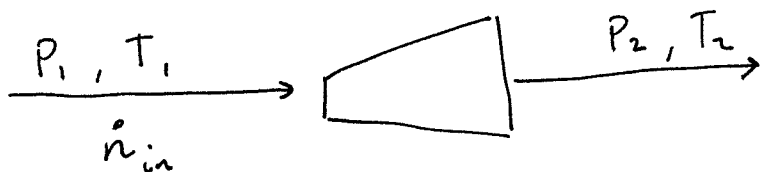
The ideal gas heat capacity for this gas is:

$$\frac{c_{p,m}^{\text{ideal}}}{R} = A + BT$$

where  $A$  and  $B$  are known constants, and  $T$  is in K.

Derive an expression for the power generated by the turbine per mole of gas,  $w_{s,m} = \frac{\dot{W}_s}{\dot{n}_1}$ .

Find  $w_{s,m}$  in terms of the following known quantities:  $P_1, P_2, T_1, T_2, a, b, A, B, R$ .



Mole balance:  $\frac{dn}{dt} = 0 = \dot{n}_{in} - \dot{n}_{out}$

$$\rightarrow \dot{n}_{in} = \dot{n}_{out} = \dot{n}$$

1st Law:

$$\frac{d}{dt}(U + E_k + E_p) = 0 = \dot{n}_{in} h_{m,1} - \dot{n}_{out} h_{m,2} + \cancel{\dot{Q}}_0 + \dot{W}_s$$

$$\dot{W}_s = \dot{n}(h_{m,2} - h_{m,1})$$

$$w_{s,m} = \frac{\dot{W}_s}{\dot{n}} = h_{m,2} - h_{m,1}$$

$$\Delta h_m = \int_{"1"}^{"2"} dh_m$$

where  $dh_m = C_{p,m} dT + \left[ v_m - T \left( \frac{\partial v_m}{\partial T} \right)_P \right] dP$

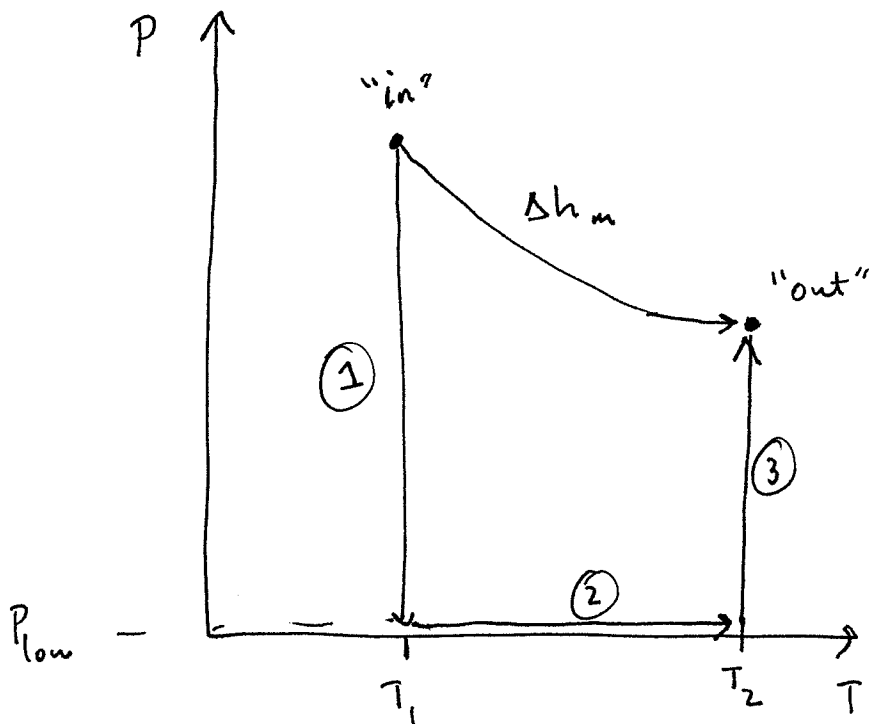
$$P = \frac{1}{v_m - b} \left( RT - \frac{aP}{\sqrt{T}} \right)$$

$$v_m = \frac{RT}{P} - \frac{a}{\sqrt{T}} + b$$

$$\left( \frac{\partial v_m}{\partial T} \right)_P = \frac{R}{P} + \frac{a}{2T^{3/2}}$$

$$\begin{aligned} \left[ v_m - T \left( \frac{\partial v_m}{\partial T} \right)_P \right] &= \left( \frac{RT}{P} - \frac{a}{\sqrt{T}} + b \right) - \left( \frac{RT}{P} + \frac{a}{2\sqrt{T}} \right) \\ &= b - \frac{3a}{2\sqrt{T}} \end{aligned}$$

$$\rightarrow dh_m = C_{p,m} dT + \left( b - \frac{3a}{2\sqrt{T}} \right) dP$$



$$\begin{aligned} \Delta h_m &= \Delta h_{m,1} \\ &+ \Delta h_{m,2} \\ &+ \Delta h_{m,3} \end{aligned}$$

$$\textcircled{1} : \Delta h_{m,1} = \int_{P_1}^{P_{low}} \left( b - \frac{3a}{2\sqrt{T_1}} \right) dP$$

$$\Delta h_{m,1} = b(P_{low} - P_1) - \frac{3a}{2\sqrt{T_1}} (P_{low} - P_1)$$

$$\Delta h_{m,1} = -bP_1 + \frac{3a}{2} \frac{P_1}{\sqrt{T_1}}$$

$$\textcircled{3} : \Delta h_{m,3} = \int_{P_{low}}^{P_2} \left( b - \frac{3a}{2\sqrt{T_2}} \right) dP$$

$$\Delta h_{m,3} = bP_2 - \frac{3a}{2} \frac{P_2}{\sqrt{T_2}}$$

$$\textcircled{2} \quad \Delta h_{m,2} = R \int_{T_1}^{T_2} [A + BT] dT$$

$$\Delta h_{m,2} = AR(T_2 - T_1) + \frac{BR}{2}(T_2^2 - T_1^2)$$

$$w_{s,m} = \Delta h_{m,1} + \Delta h_{m,2} + \Delta h_{m,3}$$

$$w_{s,m} = AR(T_2 - T_1) + \frac{BR}{2}(T_2^2 - T_1^2) + b(P_2 - P_1) - \frac{3a}{2} \left( \frac{P_2}{\sqrt{T_2}} - \frac{P_1}{\sqrt{T_1}} \right)$$

Name \_\_\_\_\_

2. (35 points) You need to find the enthalpy of vaporization of a fluid at 500 K. The following equilibrium saturation pressure measurements have been made: (1) the saturation pressure is 0.2 bar at 400 K, and (2) the saturation pressure is 3 bar at 550 K. The following heat capacity data are known for the liquid (L) and vapor (V) phase:

$$c_{p,m}^L = 40 \text{ [J/mol-K]}$$
$$c_{p,m}^V = 30 + 0.05T \text{ [J/mol-K]}$$

You may assume that the vapor phase is an ideal gas in this problem. Note that  $\Delta h_m^{\text{vap}} = h_m^V - h_m^L$ , where  $h_m^V$  and  $h_m^L$  are the molar enthalpies of the vapor and liquid phase, respectively.

- a) (15 points) Calculate the enthalpy of vaporization assuming that  $\Delta h_m^{\text{vap}}$  is a constant.
- b) (20 points) Calculate  $\Delta h_m^{\text{vap}}$  at 500 K, now accounting for the temperature variation of  $\Delta h_m^{\text{vap}}(T)$ .

$$a) \quad \frac{dP}{dT} = \frac{h_m^v - h_m^L}{T(v_m^v - v_m^L)} = \frac{\Delta h_m^{vap}}{T(v_m^v - v_m^L)}$$

$$v_m^v - v_m^L \approx v_m^v$$

$$v_m^v = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta h_m^{vap}}{RT^2/P}$$

If  $\Delta h_m^{vap}$  is constant

$$\int_{P_1}^{P_2} \frac{1}{P} dP = \int_{T_1}^{T_2} \frac{\Delta h_m^{vap}}{RT^2} dT$$

$$P_1 = 0.2 \text{ bar}, P_2 = 3 \text{ bar}$$

$$T_1 = 400 \text{ K}, T_2 = 550 \text{ K}$$

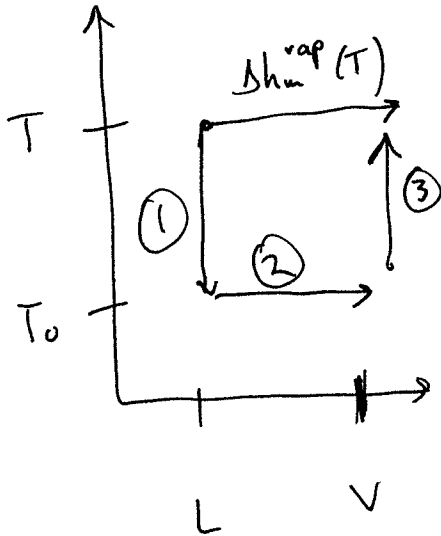
$$\ln\left(\frac{P_2}{P_1}\right) = - \frac{\Delta h_m^{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta h_m^{vap} = - \frac{R \ln\left(\frac{P_2}{P_1}\right)}{\left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$

$$\Delta h_m^{vap} = 33021 \text{ J/mol} = 33 \text{ kJ/mol}$$



b)  $\Delta h_m^{vap} = \Delta h_m^{vap}(T)$



$$\begin{aligned}\Delta h_m^{vap}(T) &= \Delta h_m^{vap}(T_0) \\ &+ \int_{T_0}^T c_{p,m}^L dT \\ &+ \int_{T_0}^T c_{p,m}^V dT\end{aligned}$$

$$\begin{aligned}\Delta h_m^{vap} &= \Delta h_m^{vap}(T_0) \\ &+ \int_{T_0}^T (c_{p,m}^V - c_{p,m}^L) dT\end{aligned}$$

$$\Delta h_m^{vap} = \Delta h_m^{vap}(T_0) + \int_{T_0}^T (-10 + 0.05T) dT$$

$$\begin{aligned}\Delta h_m^{vap} &= \Delta h_m^{vap}(T_0) - 10(T - T_0) \\ &+ 0.025(T^2 - T_0^2)\end{aligned}$$

Claapeyron:

$$\frac{dP}{dT} = \frac{\Delta h_m^{vap}(T_0) - 10(T - T_0) + 0.025(T^2 - T_0^2)}{RT^2/P}$$

Let  $T_0 = T_1$

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \left( \frac{\Delta h_m^{vap}(T_1) + 10T_1 - 0.025T_1^2}{RT^2} \right) dT$$

$$- \int_{T_1}^{T_2} \frac{10}{RT} dT + \frac{0.025}{R} \int_{T_1}^{T_2} dT$$

$$R \ln\left(\frac{P_2}{P_1}\right) = - \left[ \Delta h_m^{vap}(T_1) + 10T_1 - 0.025T_1^2 \right] \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$- 10 \ln\left(\frac{T_2}{T_1}\right) + 0.025(T_2 - T_1)$$

$$\Delta h_m^{vap}(T_1) = - \left( \frac{R \ln \frac{P_2}{P_1} + 10 \ln \frac{T_2}{T_1} - 0.025(T_2 - T_1)}{\frac{1}{T_2} - \frac{1}{T_1}} \right)$$

$$- 10T_1 + 0.025T_1^2$$

$$\Delta h_m^{\text{vap}}(T_1 = 400 \text{ K}) = 32,192 \text{ J/mol} = 32.2 \text{ kJ/mol}$$

$$\begin{aligned} \therefore \Delta h_m^{\text{vap}}(T = 500 \text{ K}) &= \Delta h_m^{\text{vap}}(T_1) \\ &\quad - 10(T - T_1) \\ &\quad + 0.025(T^2 - T_1^2) \end{aligned}$$

$$\text{where } T_1 = 400 \text{ K}$$

a

$$T = 500 \text{ K}$$

$$\Delta h_m^{\text{vap}}(T = 500 \text{ K}) = 33,442 \text{ J/mol} = 33.4 \text{ kJ/mol}$$

Name \_\_\_\_\_

3. (30 points) You are the Sr. Gatorade Engineer for the Cleveland Guardians and are responsible for ensuring the team has enough blue Gatorade for the season. To achieve this, you have tasked the engineers on your team with developing an expression for the molar volume of a mixture of water (component 1) and Gatorade concentrate (component 2). One of your colleagues has developed the following model for the molar volume of the binary liquid sports drink mixture:

$$v_m = Ax_1 + Bx_2 + Cx_1x_2^2$$

where  $A$ ,  $B$ , and  $C$  are known constants.

- a) (10 points) What is the pure species molar volume for Gatorade concentrate (species 2),  $v_{m,2}$ ? Express your answer in terms of known constants  $A$ ,  $B$ , and  $C$ .
- b) (20 points) Derive an expression for the partial molar volume of Gatorade concentrate,  $\bar{V}_2$ , in terms of  $x_1$ , as well as the known constants  $A$ ,  $B$ , and  $C$ .
- c) **Bonus** (10 extra points, no partial credit) You are skeptical about whether your colleague's proposed model for  $v_m$  is consistent with basic thermodynamics. Is the proposed model thermodynamically possible? Justify your evaluation mathematically.

$$a) \quad v_{m,2} = v_m(x_1=0, x_2=1)$$

$$\boxed{v_{m,2} = B}$$

$$b) \quad \bar{V}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{T, P, n_1}$$

$$V = (n_1 + n_2) v_m = A n_1 + B n_2 + \frac{C n_1 n_2^2}{(n_1 + n_2)^2}$$

$$\bar{V}_2 = \frac{\partial}{\partial n_2} \left[ A n_1 + B n_2 + \frac{C n_1 n_2^2}{(n_1 + n_2)^2} \right]_{T, P, n_1}$$

$$\bar{V}_2 = B + C \left[ \frac{(n_1 + n_2)^2 (2 n_1 n_2) - 2 (n_1 + n_2) n_1 n_2^2}{(n_1 + n_2)^4} \right]$$

$$\bar{V}_2 = B + 2C \left[ x_1 x_2 - x_1 x_2^2 \right]$$

$$\bar{V}_2 = B + 2C x_1 \left[ (1 - x_1) - (1 - x_1)^2 \right]$$

$$\bar{V}_2 = B + 2C x_1 \left[ 1 - x_1 - 1 + 2x_1 - x_1^2 \right]$$

$$\boxed{\bar{V}_2 = B + 2C (x_1^2 - x_1^3)}$$

c) G-D at const  $T, P$ :

$$\sum_i x_i d\bar{V}_i = 0$$

need  $\bar{V}_1$

$$\bar{V}_1 = \left( \frac{\partial V}{\partial n_1} \right)_{T, P, n_2} = \frac{\partial}{\partial n_1} \left[ A n_1 + B n_2 + \frac{C n_1 n_2^2}{(n_1 + n_2)^2} \right]_{T, P, n_2}$$

$$\bar{V}_1 = A + C \left[ \frac{(n_1 + n_2)^2 n_2^2 - 2(n_1 + n_2) n_1 n_2^2}{(n_1 + n_2)^4} \right]$$

$$\bar{V}_1 = A + C x_2^2 (1 - 2x_1)$$

$$\bar{V}_1 = A + C (1 - x_1)^2 (1 - 2x_1)$$

$$\bar{V}_1 = A + C (1 - 2x_1 + x_1^2) (1 - 2x_1)$$

$$\bar{V}_1 = A + C (1 - 2x_1 - 2x_1 + 4x_1^2 + x_1^2 - 2x_1^3)$$

$$\bar{V}_1 = A + C (1 - 4x_1 + 5x_1^2 - 2x_1^3)$$

$$x_1 \frac{d\bar{V}_1}{dx_1} + x_2 \frac{d\bar{V}_2}{dx_1} = 0 \quad \text{if valid}$$

$$\frac{d\bar{V}_1}{dx_1} = C(-4 + 10x_1 - 6x_1^2)$$

$$\frac{d\bar{V}_2}{dx_1} = 2C(2x_1 - 3x_1^2)$$

$$x_1 \frac{d\bar{V}_1}{dx_1} + (1-x_1) \frac{d\bar{V}_2}{dx_1} = 0 \quad \text{if valid}$$

$$x_1(-4 + 10x_1 - 6x_1^2) + 2(1-x_1)(2x_1 - 3x_1^2)$$

$$= (-4x_1 + 10x_1^2 - 6x_1^3) + (2x_1 - 3x_1^2 - 2x_1^2 + 3x_1^3)$$

$$= -4x_1 + 4x_1 + 10x_1^2 - 6x_1^2 - 4x_1^2 - 6x_1^3 + 6x_1^3$$

$$= (-4x_1 + 4x_1) + (10x_1^2 - 6x_1^2 - 4x_1^2) + (-6x_1^3 + 6x_1^3)$$

$$= 0 \quad (\checkmark)$$

satisfies G-D eqn,

thermodynamically  
valid.