

Name: \_\_\_\_\_

Student No.: \_\_\_\_\_

### CHEE210 Winter 2010

Instructor: Dr. Brant A. Peppley, P.Eng.

Date: Wednesday, 17 March 2010.

Answer all **four** questions on the pages provided. Use the back of pages if necessary being sure to mark the problem number and section on the additional work. Write your name and student number on each page. (Time: **60 minutes**. Total number of marks: 40. Plan time accordingly)

1. \_\_\_\_\_/10      2. \_\_\_\_\_/10      3. \_\_\_\_\_/10      4. \_\_\_\_\_/10 = \_\_\_\_\_/40

Temperature: **T (K) = T (°C) + 273.15**

Universal Gas Constant **R = 8.314 J mol<sup>-1</sup> K<sup>-1</sup> = 8.314 L kPa mol<sup>-1</sup> K<sup>-1</sup>**

**R = 82.06 cm<sup>3</sup> atm mol<sup>-1</sup> K<sup>-1</sup> = 0.08206 L atm mol<sup>-1</sup> K<sup>-1</sup>**

1 watt = 1 joule per sec      1 bar = 100 kPa

1 kWh = 1000 W × 3600 s = 3.6 MJ

Marks

1. Calculate the compressibility factor, *Z*, and the specific volume, *V*, for ethylene at 25°C and 12 bar using the truncated virial equation.

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT} \quad (10)$$

Use the generalized Pitzer correlations (refer to equation sheets attached).

For ethylene from Table B of text:

$\omega = 0.087$ ,  $T_C = 282.3 \text{ K}$ ,  $P_C = 50.40 \text{ bar}$ ,  $Z_C = 0.281$ .

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2. Estimate the residual properties ,  $H^R$  and  $S^R$  using the method of your choice for methane at 250 K and 90 bar. (Refer to equation sheets)

For methane (From Table B of text)

(10)

Molar mass = 16.043, acentric factor,  $\omega = 0.012$ ,  $T_C = 190.6$  K,  $P_C = 45.99$  bar,  
 $Z_C = 0.286$  and  $V_C = 98.6$  cm<sup>3</sup> mol<sup>-1</sup>

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3. Using the Gibbs Equations the Maxwell's Equations and the fundamental definitions of  $C_v$  and  $dU$  to show the derivation of

$$dS = C_v \frac{dT}{T} + \left( \frac{\partial P}{\partial T} \right)_v dV$$

(Hint start with the expansion:  $dS = \left( \frac{\partial S}{\partial T} \right)_v dT + \left( \frac{\partial S}{\partial V} \right)_T dV$ ) (10)

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4. Consider the heating of a house by a furnace, which serves as a heat-source reservoir at a high temperature  $T_F$ . The house acts as a heat-sink reservoir at constant temperature  $T$ , and heat  $Q$  must be added to the house during a particular time interval to maintain this temperature. All the heat  $Q$  could be transferred directly from the furnace to the house, as per the usual practice. However, a third heat reservoir is also available, namely, the surroundings at temperature,  $T_s$ , which can serve as another heat source (using a heat pump). Given that the temperature of the furnace is  $T_F = 840$  K, the temperature of the house is  $T = 295$  K and the temperature of the surroundings is  $T_s = 270$  K and  $Q=1000$  kJ, determine the minimum amount of heat,  $Q_F$  from the furnace which must be extracted from the heat-source reservoir (furnace) at  $T_F$  to maintain the temperature  $T$ . No other sources of energy are available and the house can be considered a closed system with no air exchange. Steady-state energy and entropy balance should both be used.

(Hint: Recall that for isothermal transfer of heat,  $\Delta S = \frac{Q}{T}$  and that for a reversible process  $S_{\text{gen}} = 0 = \Delta S_{\text{Total}}$ ) (10)

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## Equation Sheet for Midterm 2

## Compressibility Factor and Virial Equation of State

$$Z = \frac{V_{\text{Real}}}{V_{\text{Ideal}}} \quad PV_{\text{Real}} = ZRT$$

$$PV_{\text{Real}} = ZRT = RT[1 + B'P + C'P^2 + D'P^3 + \dots]$$

$$PV_{\text{Real}} = ZRT = RT\left[1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots\right]$$

$$B' = \frac{B}{RT}, \quad C' = \frac{C - B^2}{(RT)^2}, \quad D' = \frac{D - 3BC - 2B^3}{(RT)^3}$$

## Reduced Variables, Corresponding States and Generalized Correlations

$$P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}, \quad V_r = \frac{V}{V_c}$$

Table 3.1: Parameter Assignments for Equations of State

For use with Eqs. (3.49) through (3.56)

Eq. of State	$\alpha(T_r)$	$\sigma$	$\epsilon$	$\Omega$	$\Psi$	$Z_c$
vdW (1873)	1	0	0	1/8	27/64	3/8
RK (1949)	$T_r^{-1/2}$	1	0	0.08664	0.42748	1/3
SRK (1972)	$\alpha_{\text{SRK}}(T_r; \omega)^\dagger$	1	0	0.08664	0.42748	1/3
PR (1976)	$\alpha_{\text{PR}}(T_r; \omega)^\ddagger$	$1 + \sqrt{2}$	$1 - \sqrt{2}$	0.07780	0.45724	0.30740

$^\dagger \alpha_{\text{SRK}}(T_r; \omega) = \left[1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - T_r^{1/2})\right]^2$   
 $^\ddagger \alpha_{\text{PR}}(T_r; \omega) = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{1/2})\right]^2$

## Cubic Equations of State

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (\text{van der Waals EOS})$$

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)} \quad (\text{General Cubic EOS})$$

$$a(T) = \Psi \frac{\alpha(T_r)R^2T_c^2}{P_c}, \quad b = \Omega \frac{RT_c}{P_c}$$

## Pitzer Correlations

$$Z = Z^0 + \omega Z^1,$$

$$Z^0 = 1 + B^0 \frac{P_r}{T_r}, \quad Z^1 = B^1 \frac{P_r}{T_r},$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}, \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

## Other Equations

For saturated liquids      Molar heat capacity

$$V^{\text{sat}} = V_c Z_c^{(1-T_r)^{2/7}} \quad \frac{C_p^{\text{ig}}}{R} = A + BT + CT^2 + D/T^{-2}$$

## Entropy Equations and Second Law

$$\eta = 1 - \frac{|Q_c|}{|Q_H|} = 1 - \frac{|T_c|}{|T_H|} \quad (\text{Carnot Efficiency})$$

$$dS \equiv \left(\frac{\delta Q}{T}\right)_{\text{rev}}, \quad \oint \left(\frac{\delta Q}{T}\right)_{\text{rev}} = 0, \quad \oint \left(\frac{\delta Q}{T}\right)_{\text{irrev}} < 0$$

$$TdS = dH - VdP, \quad TdS = dU + PdV$$

## Derived equations

$$\frac{\Delta S}{R} = \int_{T_1}^{T_2} \frac{C_p^{\text{ig}}}{R} \frac{dT}{T} - \ln\left(\frac{P_2}{P_1}\right) \quad (\text{ideal gas})$$

$$\frac{\Delta S}{R} = \int_{T_1}^{T_2} \frac{C_p}{R} \frac{dT}{T} \quad (\text{solid or liquid, const. P})$$

$$\Delta S = \frac{\Delta H_{\text{transition}}}{T_{\text{Transition}}} \quad (\text{phase change})$$

$$\Delta S_{\text{Total}} = 0 \quad (\text{for a reversible process})$$

$$\Delta S_{\text{Total}} > 0 \quad (\text{spontaneous, irreversible})$$

Entropy Balance (note entropy is not conserved)

$$\frac{dS_{\text{CV}}}{dt} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} + \Delta(\dot{m}S)_{\text{fs}} = \dot{S}_{\text{gen}} \geq 0$$

$$\Delta(\dot{m}S)_{\text{fs}} = \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} + \dot{S}_{\text{gen}} \quad (\text{steady state})$$

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### Gibbs Equations and Maxwell's Equations

$$\begin{aligned} dU &= TdS - PdV \\ dH &= TdS + VdP - PdV - SdT \\ dG &= VdP - SdT \end{aligned}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P,$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \quad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

### Expressions Derived from Gibbs and Maxwell's

$$dH = C_p dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP \quad (\text{fluids, const compn})$$

$$dS = \frac{C_p}{T} dT - \left( \frac{\partial V}{\partial T} \right)_P dP$$

$$dH = C_p dT + [V(1 - \beta T)] dP \quad (\text{liquids})$$

$$dS = \frac{C_p}{T} dT - \beta V dP$$

$$dH^{ig} = C_p^{ig} dT \quad (\text{ideal gases})$$

$$dS^{ig} = \frac{C_p^{ig}}{T} dT - \frac{R}{P} dP$$

### Thermodynamic Properties of Fluids and Residual Properties

$$\frac{H}{RT} = -T \left[ \frac{\partial (G/RT)}{\partial T} \right]_P, \quad \frac{S}{R} = \frac{H}{RT} - \frac{G}{RT}$$

$$H^R = H - H^{ig} \quad S^R = S - S^{ig} \quad V^R = V - V^{ig} \quad \text{etc ...}$$

$$\frac{H^R}{RT} = -T \left[ \frac{\partial (G^R/RT)}{\partial T} \right]_P, \quad \frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT}$$

$$\frac{G^R}{RT} = \int_0^P \frac{(Z-1)}{P} dP, \quad \frac{H^R}{RT} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P},$$

$$\frac{S^R}{R} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P \frac{(Z-1)}{P} dP$$

$$H = H_o^{ig} + \int_{T_o}^T C_p^{ig} dT + H^R$$

### Using Redlich-Kwong

$$\frac{H^R}{RT} = Z - 1 - \frac{7.4}{T_r^{1.5}} \ln \left( 1 + \frac{0.08664 P_r}{Z T_r} \right)$$

$$\frac{S^R}{R} = \ln \left( Z - \frac{0.08664 P_r}{T_r} \right) - \frac{2.467}{T_r^{1.5}} \ln \left( 1 + \frac{0.08664 P_r}{Z T_r} \right)$$

### Using Virial Equation and Pitzer Correlations

$$\frac{H^R}{RT_c} = P_r \left[ B^0 - \frac{0.675}{T_r^{1.6}} + \omega \left( B^1 - \frac{0.722}{T_r^{4.2}} \right) \right]$$

$$\frac{S^R}{R} = -P_r \left[ \frac{0.675}{T_r^{2.6}} + \omega \left( \frac{0.722}{T_r^{5.2}} \right) \right]$$

$$S = S_o^{ig} + \int_{T_o}^T \frac{C_p^{ig}}{T} dT - R \ln \left( \frac{P}{P_o} \right) + S^R$$

Where  $T_o$  and  $P_o$  are reference conditions where gas behaves ideally (e.g.,  $H^R = 0$  and  $S^R = 0$ )

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Equation Sheet for Midterm 1 (for reference)  
**First Law General**

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

$$\Delta U^t = Q + W$$

$$W = -\int_{V_1}^{V_2} P_{ext} dV^t$$

$$\oint \delta Q_{cycle} = -\oint \delta W_{cycle}$$

where  $\oint$  means to integrate around a cycle

$$H = U + PV$$

**Phase Rule**

$$F = 2 - \pi + N$$

**Mass and Energy Balance**

$$\frac{dm_{cv}}{dt} + \Delta(\rho Au) = 0$$

$$\Delta(\rho Au) = 0 \quad (\text{steady state})$$

$$\frac{d(mU)_{cv}}{dt} = \dot{Q} + \dot{W} - \Delta \left[ \left( H + \frac{u^2}{2} + zg \right) \dot{m} \right]_{fs}$$

$$\dot{Q} + \dot{W} = \Delta \left[ \left( H + \frac{u^2}{2} + zg \right) \dot{m} \right]_{fs} \quad (\text{steady state})$$

**Ideal Gas**

$$PV = RT \quad dW = -P dV$$

$$C_p = C_v + R \quad dU = C_v dT \quad dH = C_p dT$$

$$dQ = C_v dT + PdV$$

$$dQ = C_v dT + RT \frac{dV}{V} \quad dW = -RT \frac{dV}{V}$$

$$dQ = C_p dT - RT \frac{dP}{P} \quad dW = -RdT + RT \frac{dP}{P}$$

$$dQ = \frac{C_v}{R} V dP + \frac{C_p}{R} P dV$$

**Adiabatic ( $C_p$  and  $C_v$  must be constant with T)**

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad T_1 P_1^{\frac{1-\gamma}{\gamma}} = T_2 P_2^{\frac{1-\gamma}{\gamma}}$$

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \quad \gamma = \frac{C_p}{C_v}$$

$$W = \frac{(P_2 V_2 - P_1 V_1)}{\gamma - 1}$$

**Isothermal**

$$Q = -W = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2}$$

**Isobaric**

$$Q = \Delta H = \int_1^2 C_p dT \quad W = -R(T_2 - T_1)$$

**Isochoric**

$$Q = \Delta U = \int_1^2 C_v dT$$