

**10.213 Chemical Engineering Thermodynamics  
Spring 2002**

**Problem Set D**

Due Wednesday, March 6, 2002 in lecture

Announcement: Test 1 (open book/open notes) will be on Friday, March 8 from 10-11 am..

Coverage will be class materials covered through this problem set and including the lecture on Mon, March 4: Topics include materials balances, ideal gas processes, PVT of real gases, enthalpies for ideal systems, entropy, etc.

Problem 13

A rigid vessel (Figure A) includes two gases that are separated by a freely moving, infinitely thin, thermally conductive partition that slides along the horizontal direction to accommodate any differences in pressure. In the vessel, the right side ( $600 \text{ cm}^3$ ) contains 2 moles of propane ( $\text{C}_3\text{H}_8$ ) at  $285 \text{ }^\circ\text{C}$ , and the left side contains 5 moles of dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). The system is at equilibrium. Determine the volume occupied by the dichloromethane.

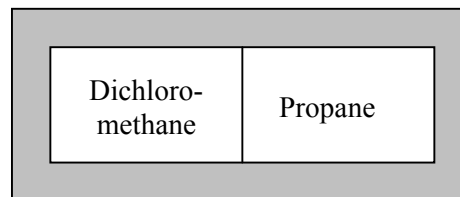


Figure A (Note: volumes of propane and dichloromethane are shown the same for purposes only of illustration)

Under these conditions, the gases do not behave ideally. Their behaviors are adequately described by the Redlich-Kwong equation and generalized correlations.

Problem 14

One mole of an ideal gas is compressed isothermally but irreversibly at  $130 \text{ }^\circ\text{C}$  from 2.5 to 6.5 bar in a piston/cylinder device. The work required is 30% greater than the work of a reversible isothermal compression. The heat transferred from the gas during the compression flows to a heat reservoir at  $25 \text{ }^\circ\text{C}$ . Calculate the entropy changes of the gas, the heat reservoir, and  $\Delta S_{\text{total}}$ .

Problem 15

a) Prove that: 
$$dS = \frac{C_v}{T} \left( \frac{\partial T}{\partial P} \right)_V dP + \frac{C_p}{T} \left( \frac{\partial T}{\partial V} \right)_P dV$$

b) Determine  $dS$  for an ideal gas from part a) and show that it simplifies to the familiar:

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

c) Prove that 
$$dU = \left[ C_p - P \left( \frac{\partial V}{\partial T} \right)_P \right] dT - \left[ T \left( \frac{\partial V}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial P} \right)_T \right] dP$$

d) Determine an expression based on part c) for  $dU$  as a function of ( $C_p$ ,  $P$ ,  $V$ ,  $T$ ,  $Z$ ) for a real gas that obeys the equation  $PV = ZRT$ . Note that  $Z = f(P, V, T)$ .

e) Determine  $dU$  for an ideal gas using the expression in part c).

### Problem 16

If 1 mole of ethylene at 500 °C and 1 bar is contacted with 2 moles of nitrogen at 25 °C and 1 bar and allowed to reach thermal equilibrium under isobaric conditions, determine  $\Delta S$  for the process. Consider both gases to behave ideally and assume that the gases remain in separated vessels (i.e., do not mix).

### Additional Practice Problem (not to be handed in)

#### Practice Problem P6

N moles of an ideal gas initially at  $(P_0, V_0, T_0)$  undergoes two processes.

- In the first, it is expanded isothermally to  $(P_1, V_1, T_0)$ . Calculate the change in entropy assuming that the heat capacity of the gas is constant.
- In the second process, the gas undergoes two steps. It is expanded reversibly at constant pressure to  $(P_0, V_1, T_1)$  followed by heating at constant volume to  $(P_1, V_1, T_0)$ . Calculate the change in entropy for this two step process assuming that the heat capacity of the gas is constant. Compare the results for parts a) and b).
- Show how your answers would be changed if the heat capacity of the gas at constant pressure depended on temperature:  $C_p/R = A + BT + CT^2$ .

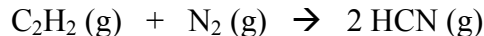
### Review Problems to Aid in Preparation for Test 1 (not to be handed in)

#### Problem PT1

What is the final temperature when heat in the amount of  $10^6$  BTU ( $1.055 \times 10^6$  kJ) is added to a 40 lbmol (18.14 kg mol) mixture of 50 mol% ethylene/50 mol% ethane initially at 500 °F (260 °C) in a steady-flow heat exchanger operating at approximately atmospheric pressure?

#### Problem PT2

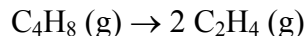
A single-pass isothermal reactor at 400 °C generates 10 mole/hr of hydrogen cyanide (HCN) from feed streams of acetylene ( $C_2H_2$ ) and nitrogen ( $N_2$ ), each 10 moles/hr, according to the reaction:



Determine the amount of heat or cooling required to maintain isothermal operation of the reactor.

#### Problem PT3

A catalytic reactor generates ethylene from butene by the reaction:



In the process, the reactor produces an equilibrium mixture that contains 20 mol% ethylene and 80 mol% butene.

- Determine the moles of ethylene produced per mole of butene entering the reactor.
- If the ethylene is separated from the butene by distillation after the reactor, and the unreacted butene is recycled back to the reactor where it is combined with a feed of butene, determine the relative molar flow rates of the entering butene and exiting ethylene streams and the recycled butene stream.