3-31 No. 1

An insulated, 10 ft^3, compartmented tank contains an ideal (but unknown) corrosive gas. The starting conditions are as follows:

	Compartment 1	Compartment 2
volume	9 ft^3	1 ft^3
pressure	1 atm	6 atm
temperature	200°C	300°C

The thin wall between compartments suddenly dissolves. What is the final pressure, final temperature,and internal energy change in the tank?

3-31 No. 2

A bicycle tire is initially pumped up with air to 100 psig. After a long ride the tire pressure is 105 psig. What is the internal energy change of the air in the tire? (Assume air is an ideal gas, Cp = 7 Btu/lbmol°F and the tire volume is unchanged at 0.01 ft^3)

3-31 No. 5

Super cooled water at -2°C is converted to ice at -2°C. The molal heat capacities of ice and water are 9 and 18 cal/g-mole°C. The heat of fusion of water is 1436 cal/mol. What are the enthalpy and entropy change for this process?

3-31 No. 6

Iodine vapor dissociates according to the equation:

$$I_2 \rightarrow 2I \qquad K = (I)^2 / (I_2)$$

The equilibrium constant for this reaction is 3992 and 0.0002 at 1000°C and 600°C respectively. What is the heat of reaction and % dissociation at 900°C?

3-32 No. 1

Calculate the entropy change when 1 lb. of ammonia is cooled from 500°F to -150°F at a constant pressure of 1 atm. Express the results in Btu/lb.°R. Calculate the absolute entropy of solid NH3 at its melting point at 1 atm. pressure in Btu/lb.°R.

NH3 data:

a = 6.5846

b = 6.1251 x 10^{-3}

c = 2. 3663 x 10^{-6}

d =-1.5981 x 10^{-9}

b.p. =-33.4 °C

m.p. = -77.7 °C

Cp(cal/mol-K) = a + bT + cT^2 + dT^3 (where T is in degrees K)

S = 46.03 cal/mol °K (absolute entropy of gas at 25°C)

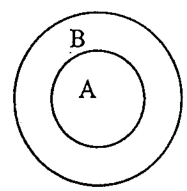
$\lambda v = 5581$ cal/g-mole
$\lambda f = 1352$ cal/g-mole
Cp(solid) = 0.502 cal/g-°K
Cp(liquid) = 1.06 cal/g-°K

3-32 No. 2
Dry sodium acetate, $NaC_2H_3O_2$, is stored and charged into a dry material feeder in an area maintained at 68°F. The dry feed is added to a jacketed mixer agitated by a 5 hp high shear impeller. This vessel also receives a stream of 55°F water at a rate calculated to produce a 9 mole% solution when drawn off at a rate of 20 gpm. The solution is then pumped with a 7 1/2 hp pump into a reactor where it must enter at 135°F. (Specific gravity of solution 1.15; specific heat of the solution 0.94 cal/g°C; specific heat of solid 0.339 cal/g°C; heat of solution -3943 cal/gm formula wgt at 25°C) Calculate the heat in Btu/hr that must be added or taken away in the mixer if this temperature requirement is to be met.

3-32 No. 5
An equimolecularmixture of hydrogen and carbon monoxide is mixed with the stoichiometric quantity of air in a closed, insulated vessel. The total pressure of the mixture is 5 atmospheres and the temperature is 25°C. The mixture is ignited by a spark plug. The oxidation of the reactants is assumed complete. Assuming all the gases are ideal, estimate (a) the maximum temperature and (b) the pressure that might be expected.

3-33. No. 9
Acetonitrile, C2H3N, is stored at a temperature of 550 F and a pressure of 4500 psia in a high pressure vessel (A) with a capacity of 0.2 cubic feet. For safety, the 0.2 ft^3 vessel is contained in a second pressure vessel. The volume of the second vessel (B) is 2 ft^3 (exclusive of the volume occupied by vessel A which it surrounds). This volume is filled with inert nitrogen at 10 atmospheres pressure. The entire assembly is maintained at 550°F. If the inner tank ruptures, what is the final pressure? The critical data and a diagram of the tanks are as follows:

	Tc K	Pc atm
N_2	126.2	33.5
C_2H_3N	548.0	47.7



7-34 No. 1
A mixture of ethane, propane, and n-butane exists at -10°C at a total pressure of 3000 mm Hg. Determine the compositions of the vapor and liquid phases if the propane and n-butane compositions are equal in the liquid phase. Vapor pressures at -10 C are (in mm Hg): ethane: 14000, propane: 2700, and n-butane: 500.

7-35. No. 1

A mixture of two high boiling organic acids is to be separated from a small amount of non-volatile carbonaceous material by continuous steam distillation in a small still operating at 212°F and 200 mmHg. The organic acid mixture is equimolar with respect to the acids whose vapor pressures are 32 and 14 mmHg at 212°F. With the following assumptions:

a. The acid mixture obeys Raoult's Law
b. The acid mixture is immiscible in water
c. The carbonaceous material has no effect on equilibrium
d. The vapor leaves in equilibrium with the liquid in the still

How many pounds of steam are required per mole of acid recovered?

7-35 No. 6

A mixture of hydrocarbons (10 mol% methane, 20 mol% ethane, 30% mol% propane, 15 mol% isobutane, 20 mol% n-butane, and 5 mol% n-pentane) is flashed into a separator at 80°F and 150 psia. Fifty percent of the mixture leaves as a liquid. What is the composition of the liquid? Equilibrium constants are as follows:

$CH_4 = 17.0$ $C_2H_6 = 3.1$ $C_3H_8 = 1.0$

i-$C_4H_{10} = 0.44$ $C_4H_{10} = 0.32$ $C_5H_{12} = 0.0986$

Bonus VLE Question:

A mixture of 70 mole % n-butane, 4 mole % water, and 26 mole % nitrogen is at 75°C and 50 psia. Antoine constants are given below:

Form: $\log_{10}Psat = A - B / (T + C)$
where T is the temperature in °C
Psat is the vapor pressure in mmHg

Compound	A	B	C
n-butane	6.85353	955.43	241.0
water	8.10765	1750.286	235.0

1. Liquid mixtures of butane and water can be characterized as:
   A. ideal
   B. non-ideal
   C. highly non-ideal
   D. cannot be characterized

2. At 50 psia, as the temperature is reduced, which of the following observations best describes the essential nature of the problem?
   A. high boilers condense first
   B. Low boilers condense first
   C. there exists a dew point
   D. there exist multiple dew points.

3. At what temperature will the first drop of liquid form?
   A. 32°C
   B. 350C
   C. 49°C
   D. 52°C

4. The composition of the fin'st drop of liquid will be:
   A. water
   B. butane
   C. nitrogen
   E. 70% butane, 4% water, 26% nitrogen

5. At 50 psia, essentially no butane will condense until the temperature is reduced below:
   A. 0°C
   B. 26°C
   C. 32°C
   D. 52°C

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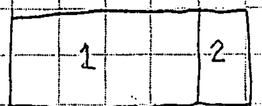
3-31 #1



Initial Conditions $V_1 = 9\ ft^3$ $\qquad V_2 = 1\ ft^3$

$P_1 = 1\ atm \qquad P_2 = 6\ atm$

$T_1 = 200°C \qquad T_2 = 300°C$

Final Conditions (3) $\qquad V_3 = V_1 + V_2 = 10\ ft^3$

$P_3 = ?$

$T_3 = ?$

Assume ideal gas $\qquad PV = nRT$

$$n_3 = n_1 + n_2 \qquad \frac{P_3 V_3}{T_3} = \frac{P_2 V_2}{T_2} + \frac{P_1 V_1}{T_1} \qquad (1)$$

2 unknowns in (1)

Internal energy change in Tm

Apply 1st Law of thermodynamics for closed systems, $\boxed{\Delta U = \cancel{Q}^{0} - \cancel{W}^{0} = 0}$

$$\Delta U = 0 = \Delta U_1 + \Delta U_2 = n_1 C_v (T_3 - T_1) + n_2 C_v (T_3 - T_2)$$

$$n_1 = \frac{P_1 V_1}{R T_1} \quad n_2 = \frac{P_2 V_2}{R T_2} \Rightarrow \frac{P_1 V_1}{R T_1} C_v (T_3 - T_1) + \frac{P_2 V_2}{R T_2} C_v (T_3 - T_2) = 0$$

Assume constant heat capacity, solve for T_3

$$T_3 = \frac{P_1 V_1 + P_2 V_2}{\frac{P_1 V_1}{T_1} + \frac{P_2 V_2}{T_2}} = \frac{(9)(1) + (6)(1)}{\frac{(9)(1)}{473.15} + \frac{(6)(1)}{573.15}} = 508.65°K = \boxed{235.5°C}$$

final temp.

From (1)

$$P_3 = \frac{T_3}{V_3}\left[\frac{P_2 V_2}{T_2} + \frac{P_1 V_1}{T_1}\right] = \frac{508.65°K}{10 ft^3}\left[\frac{(6 atm)(1 ft^3)}{573.15°K} + \frac{(1 atm)(9 ft^3)}{473.15°K}\right]$$

$$\boxed{= 1.5\ atm}$$

final pressure

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1st Law (const volume) $\Delta U = \int C_v \, dT$

Ideal Gas $PV = RT$, $T = \frac{PV}{R}$

const V, $dT = \frac{V}{R} dP \Rightarrow \Delta U = \int C_v \frac{V}{R} dP = C_v \frac{V}{R}(P_2 - P_1)$

(if C_v = const)

Ideal gas $\therefore C_v = C_p - R = 7 - 1.987 \frac{Btu}{lb\text{-}mol\,°R} = 5.013$

$$\Rightarrow \Delta U = \frac{\left(5.013 \frac{Btu}{lb\text{-}mol\,°R}\right)(0.01\ ft^3)}{10.73\ psi\ ft^3/lb\text{-}mol\,°R}(5\ psi) = \boxed{0.0234\ Btu}$$

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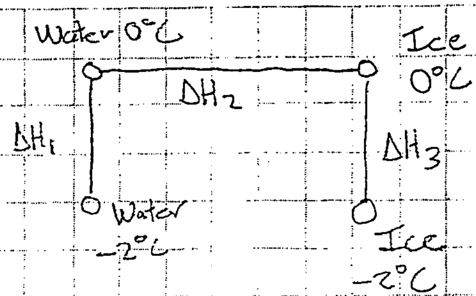

Enthalpy is a state function. Devise a path the steps of which are easily calculated.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H = \left(18 \frac{cal}{mol\,°C}\right)(2°C) + \left(-1436 \frac{cal}{mol}\right) + \left(9 \frac{cal}{mol\,°C}\right)(-2°C)$$

add heat + remove heat − remove heat −

$$\boxed{\Delta H = -1418\ cal/mol}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_1 = C_p \ln(T_2/T_1) \quad \text{(const P)}$$

$$\Delta S_2 = \Delta H_f / T \quad \text{(const T)}$$

$$\Delta S_3 = C_p \ln(T_2/T_1) \quad \text{(const P)}$$

$$\Delta S = \left(18 \frac{cal}{mol\,°C}\right)\left(\ln\left(\frac{273.15}{271.15}\right)\right) + \frac{-1436\ cal/mol}{273.15\ K} + \left(9 \frac{cal}{mol\,°C}\right)\left(\ln \frac{271.15}{273.15}\right)$$

$$\boxed{\Delta S = -5.19\ cal/mol\,°C}$$

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$$I_2 \rightarrow 2I \qquad K = \frac{(I)^2}{(I_2)}$$

$1-x \qquad 2x$

T°C	T°K	K
1000	1273	3992
600	873	0.0002

Van't Hoff Eq'n $\frac{d(\ln K)}{dT} = \frac{\Delta H_{Rxn}}{RT^2}$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{Rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ (Assume const ΔH_{Rxn})

$$\ln\left(\frac{3992}{0.0002}\right) = -\frac{\Delta H_{Rxn}}{1.987\ cal/g\text{-}mol\ K}\left(\frac{1}{1273} - \frac{1}{873}\right)$$

$$\Rightarrow \boxed{\Delta H_{Rxn} = 92\,796\ cal/mol}$$

$960°C = 1173°K$

$$\ln\left(\frac{K_2}{3992}\right) = -\frac{92\,796}{1.987}\left(\frac{1}{1173} - \frac{1}{1273}\right)$$

$$\boxed{K_2 = 175}$$

$$I_2 \rightarrow 2I$$

	I_2	$2I$	
Initial	1	0	
Final (equil)	$1-x$	$2x$	Total moles $= 1+x$

$$K = \frac{\frac{(2x)^2}{(1+x)^2}}{\frac{1-x}{1+x}} = \frac{4x^2}{(1+x)(1-x)} = \frac{4x^2}{1-x^2}$$

$$x^2(4+K) = K \qquad x = \sqrt{K/(K+4)}$$

$$x = \sqrt{\frac{175}{(175+4)}} = 0.989$$ or $\boxed{98.9\%\ \text{dissociation}}$

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SUBJECT 3-32 # 1

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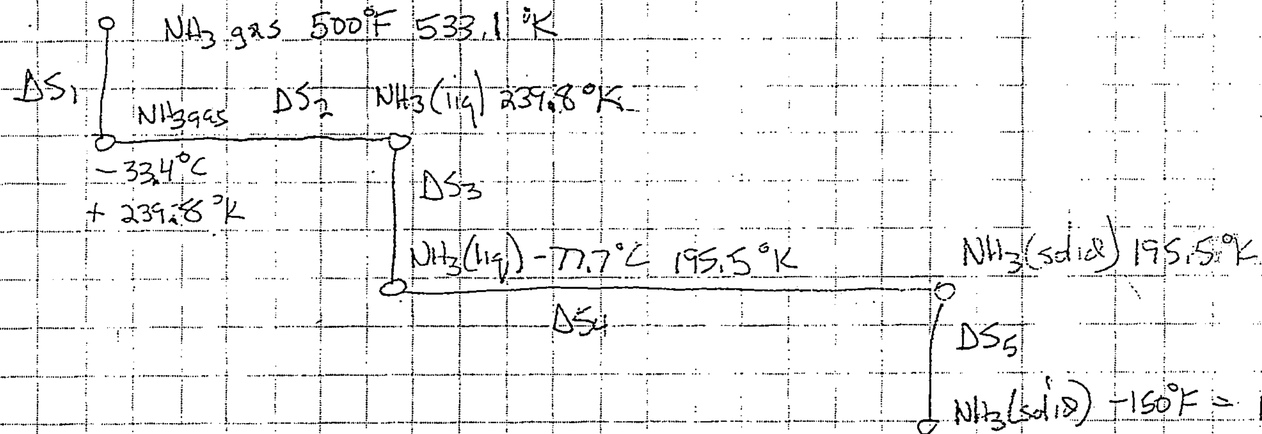
1 lb NH_3 MW = 17.032 $\frac{g}{mol}$

a) ΔS from 500°F to −150°F at 1 atm
b) Absolute entropy of $NH_{3\,solid}$ at melting pt.



$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

① $$\Delta S_1 = \int_{T_1}^{T_2} \frac{C_p}{T}\,dT = a \ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1) + c\left(\frac{T_2^2 - T_1^2}{2}\right) + d\left(\frac{T_2^3 - T_1^3}{3}\right)$$

Units not given, but should be cal/mol °K

$$\Delta S_1 = 6.5846 \ln\left(\frac{239.8}{533.1}\right) + 6.1251\times10^{-3}(239.8 - 533.1) + \frac{2.3663\times10^{-6}\left[239.8^2 - 533.1^2\right]}{2} + -1.5981\times10^{-9}\frac{\left[239.8^3 - 533.1^3\right]}{3}$$

$$\Delta S_1 = -7.2518 \frac{cal}{mol\,°K}\left(\frac{mol}{17.032\,g}\right) = -0.426 \frac{cal}{g\,K}$$

② $$\Delta S_2 = \frac{\lambda}{T} = \frac{-5581\ cal/mol}{239.8\ °K \quad 17.032\ g/mol} = -1.366\ cal/g\ °K$$

③ $$\Delta S_3 = \int_{T_1}^{T_2} \frac{C_p}{T}\,dT = C_p \ln\left(\frac{T_2}{T_1}\right) = 1.06 \frac{cal}{g\,K} \ln\left(\frac{195.5}{239.8}\right) = -0.217 \frac{cal}{g\,K}$$

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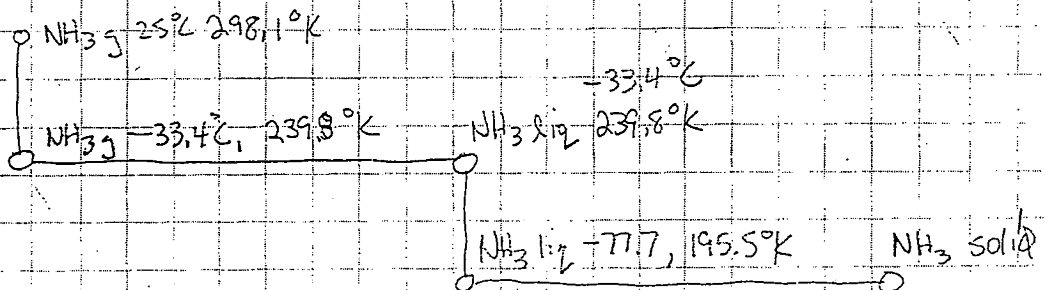
(4) $\Delta S_4 = \frac{\lambda}{T} = \frac{-1352 \text{ cal/mol}}{195.5°K \quad 17.032 \text{ g/mol}} = -0.406 \frac{\text{cal}}{\text{g K}}$

(5) $\Delta S_5 = C_p \ln\left(\frac{T_2}{T_1}\right) = 0.502 \frac{\text{cal}}{\text{g K}} \ln\left(\frac{172.0}{195.5}\right) = -0.0643 \text{ cal/g K}$

$\Delta S = \sum \Delta S_i = -2.479 \frac{\text{cal}}{\text{g°K}} = \boxed{-2.479 \frac{\text{Btu}}{\text{lb°R}}}$

(b) $S_{NH_3(s)\,-77.7°C} = S_{g(25°C)} + \Delta S$



$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$

$\Delta S_1 = a \ln\frac{T_1}{T_2} + b(T_2 - T_1) + c\,\frac{T_2^2 - T_1^2}{2} + d\,\frac{T_2^3 - T_1^3}{3}$

$\Delta S_1 = 6.5846 \ln\left(\frac{239.8}{298.1}\right) + 6.1251\times10^{-3}(239.8 - 298.1) + 2.3663\times10^{-6}\frac{[239.8^2 - 298.1^2]}{2}$

$+ (-1.5981\times10^{-9})\frac{[239.8^3 - 298.1^3]}{3}$

$\Delta S_1 = -1.8366 \text{ cal/mol K} = -0.1078 \text{ cal/g K}$

From (a) $\Delta S_2 = -1.366 \quad \Delta S_3 = -0.217 \quad \Delta S_4 = -0.406$

$\Rightarrow \Delta S = -2.097 \frac{\text{cal}}{\text{g K}}$

$S_{195.5K} = \left(46.03 \frac{\text{cal}}{\text{gmol K}}\right)\left(\frac{\text{mol}}{17.032 \text{ g}}\right) - 2.097 = 0.606 \frac{\text{cal}}{\text{g K}} = 0.606 \frac{\text{Btu}}{\text{lb°R}}$

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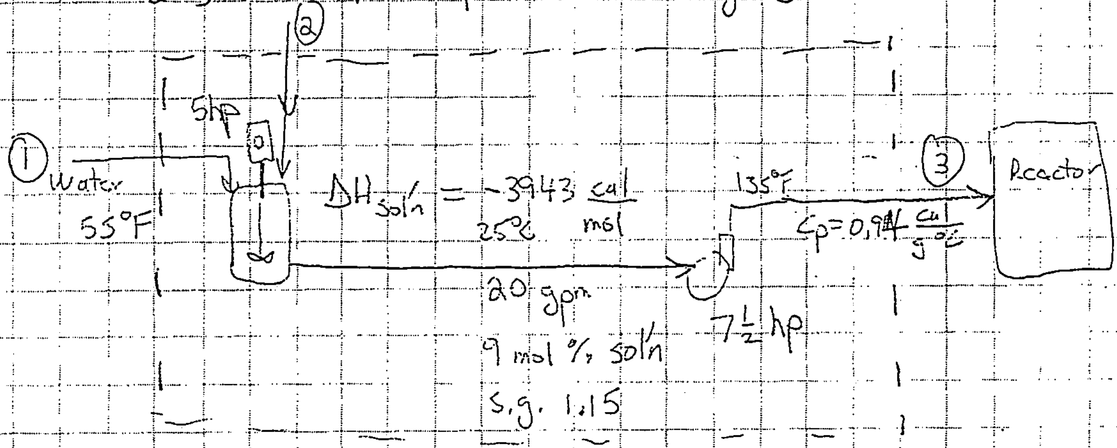
$NaC_2H_3O_2$ 68°F $C_p = 0.339\ cal/g\ °C$ M.W. = 82.04



a) Mat'l balance on mixer

$$F_{H_2O} + F_{sa} = 20\ \frac{gal}{min}(1.15)\left(8.34\ \frac{lb}{gal}\right)\frac{60\ min}{hr} = 11510\ \frac{lb\ soln}{hr}$$

$$wt\%\ s.a. = \frac{(0.09\ mol)(82.04\ g/mol)}{(0.09\ mol)(82.04) + (0.91)(18.016)} = 0.311 \text{ or } 31.1\%$$

⇒ Feed Rates s.a.: $(11510)(0.311) = 3580\ lb/hr$

H_2O: $(11510)(1-0.311) = 7930\ lb/hr$

b) Energy balance $\Delta H = Q - W$ (Flow system)

Choose reference state = 25°C = 77°F Neglect heat losses!

Calculate feed and product stream enthalpies

$$H_1\ (\text{water feed}) = (7930\ lb/hr)\left(1\ \frac{Btu}{lb\ °F}\right)(55-77\ °F) = -174500\ Btu/hr$$

$$H_2\ (\text{s.a. feed}) = (3580\ lb/hr)\left(0.339\ \frac{Btu}{lb\ °F}\right)(68-77\ °F) = -10900\ Btu/hr$$

H_3 [illegible] = (11510 lb/hr)(0.94)(135 - 77) = [illegible]

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Stream 3 (product) enthalpy must include the heat of soln

$$\Delta H_{soln} = \frac{-3943 \text{ cal}}{\text{mole}} \left| \frac{9.486\times10^{-4} \text{ Btu}}{0.23901 \text{ cal}} \right| \frac{\text{mol}}{82.04 \text{ g}} \left| \frac{453.6 \text{ g}}{\text{lb s.a.}} \right| \frac{3580 \text{ lb s.a.}}{\text{hr}} = -309\,760 \frac{\text{Btu}}{\text{hr}}$$

$$H_3 \text{ (product soln)} = \left(11510 \frac{\text{lb soln}}{\text{hr}}\right)(0.94)(135-77) - 309\,760 \frac{\text{Btu}}{\text{hr}} = 317\,770 \frac{\text{Btu}}{\text{hr}}$$

$$W = -\left(5+7\tfrac{1}{2}\right)\text{hp}\left(\frac{9.486\times10^{-4} \text{ Btu/s}}{1.341\times10^{-3} \text{ hp}}\right)\left(\frac{3600 \text{ sec}}{\text{hr}}\right) = -31\,830 \text{ Btu/hr}$$

negative because work done on system rather than by system
(Assume all mech. power input is lost to viscous dissipation - friction.)

$$Q = \Delta H + W = H_3 - H_1 - H_2 + W = 317770 - (-10900 - 174500) - 31830$$

$$\boxed{Q = 471\,340 \text{ Btu/hr}}$$ Is positive so this is heat added!

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Overall

$$H_2 + CO + O_2 + \frac{0.79}{0.21}N_2 \longrightarrow CO_2 + H_2O + \frac{0.79}{0.21}N_2$$

ΔH^0_{298}, cal/mol

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O(g) \quad -57{,}798$$

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2 \quad -67{,}635$$

$$H_2 + CO + O_2 \rightarrow H_2O + CO_2 \quad -125\,433 \text{ cal/mol}$$

$$\text{Reactants, } 25°C \xrightarrow[\Delta H^0_{298}]{} \text{Products } 25°C \xrightarrow[\Delta H^0_p]{} \text{Products at } T_{max}$$

$$\Delta H^0_{T_{max}} = \Delta H^0_{298} + \Delta H^0_p = \Delta H^0_{298} + \left[\Sigma(n\,C^0_{p\,mean})\right](T_{max} - 298)$$

From Fig 4-1 (Smith + Van Ness), estimate $C^0_{p\,mean}$ assuming $T \approx 4000°F$

CO_2 $\quad C_{p\,mean} = 13.2$ cal/g-mol °C
H_2O $\quad = 10.6$
N_2 $\quad = 8.1$

$$\Delta H^0_{T_{max}} = -125\,433 + \left[1(13.2) + 1(10.6) + \frac{0.79}{0.21}(8.1)\right](T_{max} - 298)$$

$$\Delta H_{T_{max}} = 54.256\,T_{max} - 141{,}601$$

From First Law (closed system!) $\Delta U = 0$ (not ΔH!)

Definition $H = U + PV$ and $\Delta H = \Delta U + \Delta PV$

Assume ideal gas $PV = nRT$

$$\Delta PV = \underbrace{n_2 R T_{max}}_{\text{after rxn}} - \underbrace{n_1 R T_1}_{\text{before RXN}}$$

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$$\Delta PV = 5.76(1.987)(T_{max}) - 6.76(1.987)(298)$$

$$\Delta PV = 11.445\,T_{max} - 4002.8$$

$$54.256\,T_{max} - 141{,}601 = 11.445\,T_{max} - 4002.8$$

$$\boxed{T_{max} = 3214\,K = 2940^\circ C = 5325^\circ F}$$

(Compare this to our assumed T_{max} of 4000°F to look up the $C_{p\,means}$. We could go back and try another.)

b) Estimate final pressure:

assume const V

$$\frac{P_1}{n_1 T_1} = \frac{P_2}{n_2 T_2} \qquad \frac{5}{(6.76)(298)} = \frac{P_2}{(5.76)(3214)}$$

$$\boxed{P_2 = 45.9\ atm}$$

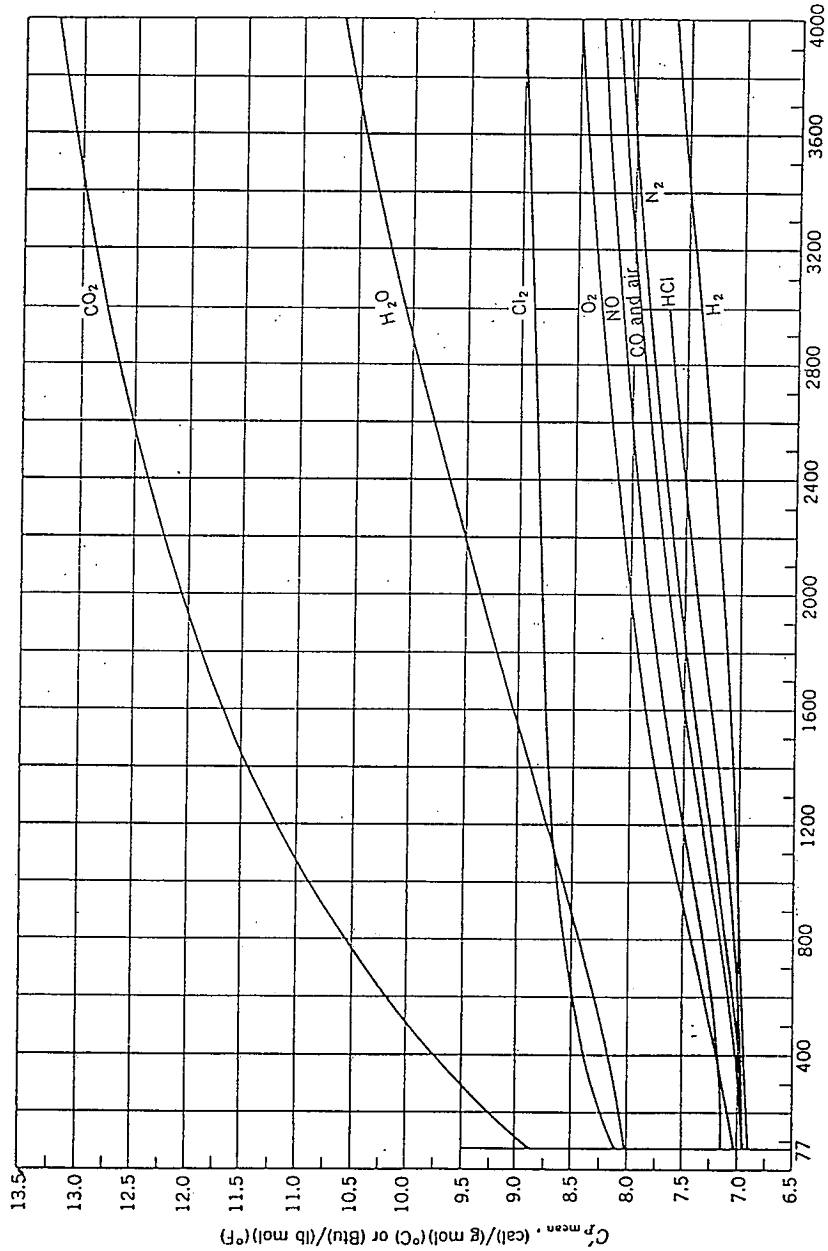

Fig. 4-1a Mean molar heat capacities of gases in the ideal-gas state. Base temperature, 77(°F). [Based mainly on data from D. D. Wagman (ed.), Selected Values of Chemical Thermodynamic Properties, *Natl. Bur. Stand. U.S. Circ.* 500, 1952.]

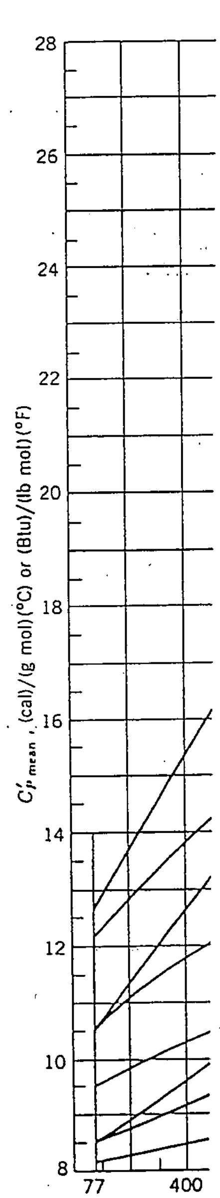

Fig. 4-1b Mean mc temperature, 77(°F). Selected Values of *Stand. Circ.* 500, 19

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SUBJECT 3-33 #9

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	T_c, K	P_c, atm
N_2	126.2	33.5
C_2H_3N	548.0	47.7

Not ideal gas, Approach:

1. Calculate T_r and P_r to get Z.
2. Determine # moles of each
3. Calculate pseudocritical T_r, P_r for mixture
4. Determine final P

$PV = znRT$ ← Empirical correlation using T_r, P_r, ω

$T_r = T/T_c$ $\quad P_r = P/P_c$ $\quad \omega$ = acentric factor

N_2: $T_r = \frac{550+460\,°R}{126.2\ °K}\left(\frac{1\,°K}{1.8\,°R}\right) = 4.45$

$P_r = \frac{10}{33.5} = 0.30$

$\Rightarrow z = 1.0$ (i.e. ideal)

C_2H_3N: $T_r = \frac{550+460}{548}\left(\frac{1}{1.8}\right) = 1.024$

$P_r = \frac{4500\ psi}{47.7\ atm}\ \frac{1\ atm}{14.7\ psi} = 6.42$

Use the generalized correlation $Z = Z^0 + \omega Z^1$

Z^0 ↑ Fig 3-12, Z^1 ← Fig 3-13) Smith & Van Ness

$Z^0 = 0.84$
$Z' = -0.24$
$\omega = 0.321$ (Appendix B)

$Z = 0.84 + 0.321(-0.24) = 0.76$

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$$n_{N_2} = \frac{PV}{ZRT} = \frac{(10\,atm)(2\,ft^3)}{(1)\left(0.73023\,\frac{atm\,ft^3}{lb\text{-}mol\,R}\right)(550+460\,°R)} = 0.0271\ lb\text{-}mol$$

$$n_{C_2H_3N} = \frac{PV}{ZRT} = \frac{(4500)(0.2)}{(0.76)(10.73)(550+460)} = 0.1093\ lb\text{-}mol$$

$$n_{TOTAL} = 0.1364\ lb\text{-}mol$$

p.277 Smith & Van Ness
(mixing rule!)
Use molar average to get pseudo-critical properties

$$P_c = \frac{0.0271}{0.1364}(33.5) + \frac{0.1093}{0.1364}(47.7) = 44.9\ atm$$

$$T_c = \ ''\ (126.2) + \ ''\ (548.0) = 464.2\ °K$$

$$T_r = \frac{1010}{(464.2)(1.8)} = 1.21$$

$$P_r = \frac{P}{P_c} = \frac{ZnRT}{P_c V} = Z\,\frac{(0.1364)(0.73023)(1010)}{(44.9)(2.2)} = 1.018\,Z$$

$$\omega = \frac{0.0271}{0.1364}\,0.04 + \frac{0.1093}{0.1364}(0.321) = 0.265$$

To find Z, assume a value and check with charts

Assume $Z = 0.9$, $P_r = 0.92 \Rightarrow Z^0 = 0.63$, $Z' = -0.02 \Rightarrow Z = 0.635$

Assume $Z = 0.75$, $P_r = 0.76 \Rightarrow Z^0 = 0.74$, $Z' = 0$, $\Rightarrow Z = 0.74$

$P_r = 0.76$, $P = P_r \cdot P_c = 0.76\,(44.9\ atm) = \boxed{34.1\ atm}$

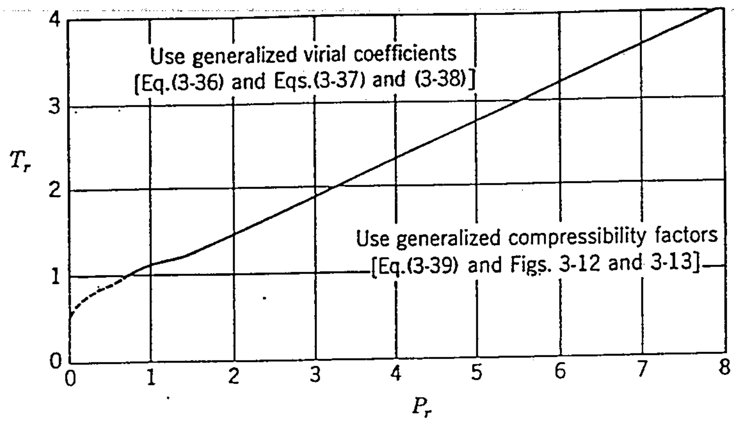

Fig. 3-11 Line defining region where generalized second virial coefficient may be used. Above $T_r = 1.2$ conforms to $V_r \approx 2$.

in Fig. 3-11. This line is based primarily on the criterion that $V/V_c \equiv V_r \geq 2$. For reduced temperatures above $T_r = 4$, there appears to be no set limitation on the pressure; however, V_r should be ≥ 2. For lower reduced temperatures the allowable pressure range decreases with decreasing temperature. A point is reached, however, at a reduced temperature of about 0.9, where the pressure range is limited by the saturation (condensation) pressure. Thus the dashed portion of the line shown in Fig. 3-11 represents the saturation curve.

The relative simplicity of this correlation does much to recommend it. Moreover, the temperature and pressure range within which it may be used covers the vast majority of applications to chemical processing. It is most accurate for nonpolar gases and least accurate for highly polar and associating molecules.

For the range of conditions lying below the line of Fig. 3-11, Pitzer proposed a correlation for the compressibility factor Z of the form

$$Z = Z^0 + \omega Z^1 \tag{3-39}$$

where Z^0 and Z^1 are complex functions of both T_r and P_r. Since $\omega = 0$ for argon, krypton, and xenon, the second term disappears, and Z^0 must be represented by the correlation of Z for these gases as a function of T_r and P_r. Thus the generalized relationship $Z^0 = f^0(T_r, P_r)$ is based on experimental PVT data for these three inert gases.

Equation (3-39) represents a simple linear relation between Z and ω for given values of T_r and P_r. Experimental data for Z plotted vs. ω at constant T_r and P_r do indeed yield straight lines, and their slopes provide values for Z^1 upon which to base the generalized function $Z^1 = f^1(T_r, P_r)$.

Correlations of Z^0 and Z^1 based on experimental data and expressed as functions of T_r and P_r are given by Figs. 3-12 and 3-13. The range of conditions covered by these charts corresponds to the area below the line of Fig. 3-11. Examples of their use appear at the end of this section.

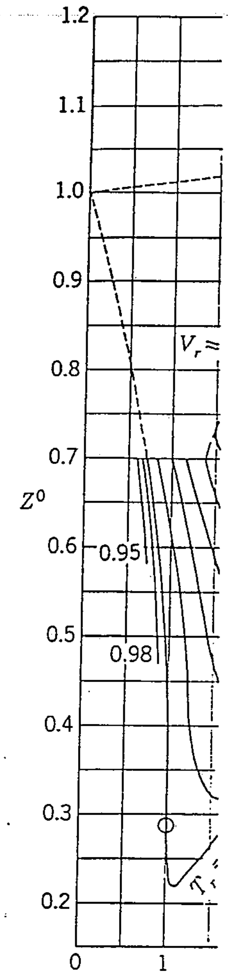

Fig. 3-12 Generalized ... and xenon from Pitzer.

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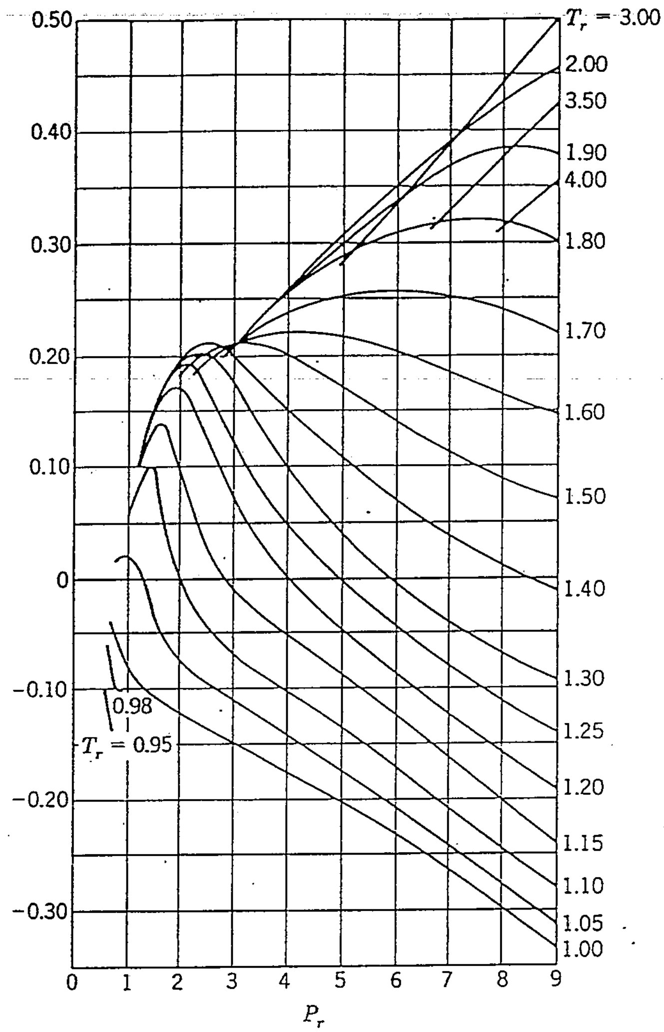


Fig. 3-13 Generalized correlation for Z^1 from Pitzer's correlation.

Example 3-6 Determine the molar volume of *n*-butane at 460(K) and 15(atm) by each of the following:

(*a*) Ideal-gas law

(*b*) A generalized correlation based on Eq. (3-36) or (3-39), whichever is appropriate

(*c*) Equation (3-29), with the experimental values $B = -265(\text{cm})^3/(\text{g mol})$ and $C = 30{,}250(\text{cm})^6/(\text{g mol})^2$

Solution

(*a*) Ideal-gas law:

$$V = \frac{RT}{P} = \frac{(82.05)(460)}{15} = 2{,}516(\text{cm})^3/(\text{g mol})$$

(*b*) A gei

$$T_r = \frac{460}{425} =$$

Since these valu
correlation for s
(3-38)

$$B^0 = -0.$$

Equation (3-36)

$$\frac{BP_c}{RT_c} = B^0$$

Then from Eq. (

$$Z = 1 - ($$

and finally,

$$V = \frac{ZRT}{P}$$

(*c*) Virial
By Eq. (3-29),

$$Z = \frac{PV}{RT} =$$

$$\frac{15V}{(82.05)(46}$$

Solution by trial
imental data, it
follows:

(*a*) Ideal-
(*b*) Gene

Example 3-7 W
volume of $2(\text{ft})^3$

(*a*) The i
(*b*) The R
(*c*) A gen

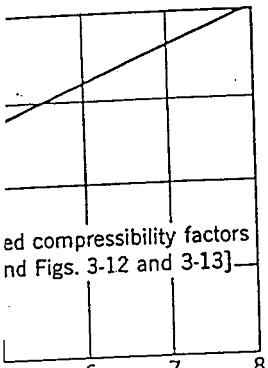
Solution

(*a*) The i

$$P = \frac{RT}{V} =$$

(*b*) The R
By Eq. (3-33*C*),

$$b = \frac{0.0867}{P_c V}$$



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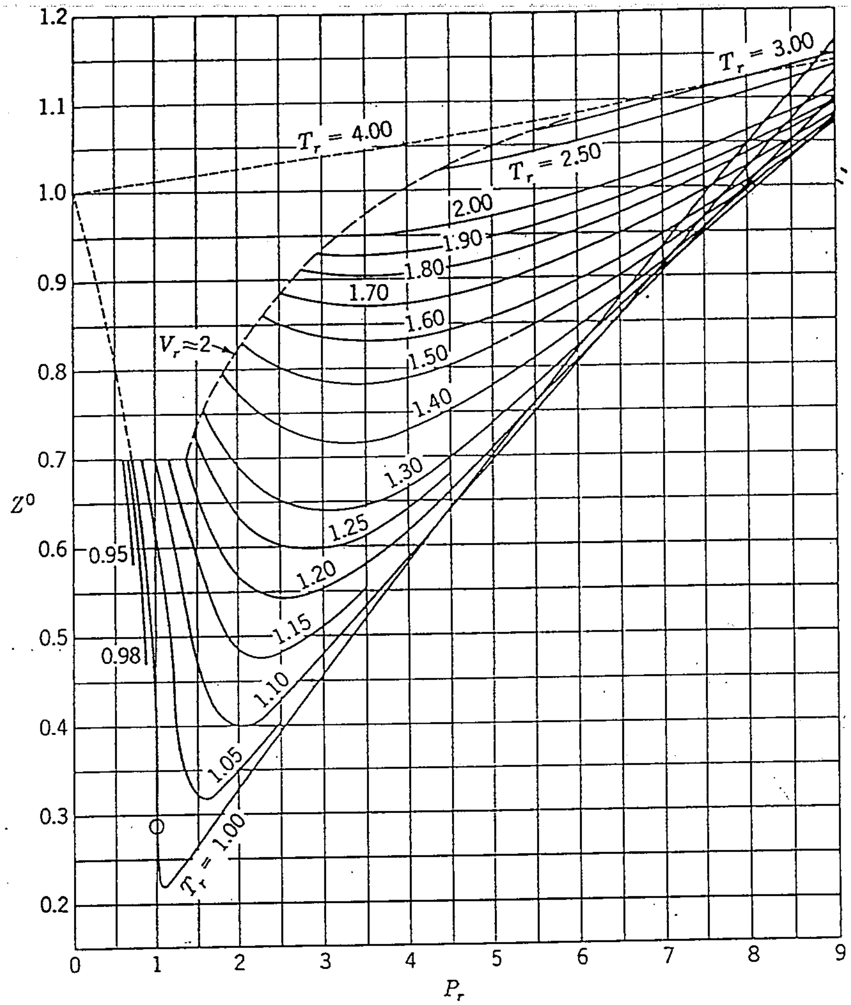

Fig. 3-12 Generalized correlation for Z^0. Based on data for argon, krypton, and xenon from Pitzer's correlation.

The Pitzer correlations provide reliable results for gases which are nonpolar or only slightly polar. An accuracy to within 3 percent can be expected. When applied to highly polar gases errors of 5 to 10 percent may result, and for gases which associate, even larger errors are possible. In addition, generalized correlations do not give good results for gases which reflect quantum effects. Helium and hydrogen are the most common of these, and fortunately reliable data are available for these gases. It should be emphasized that generalized correlations are not intended to be substitutes for reliable experimental PVT data.

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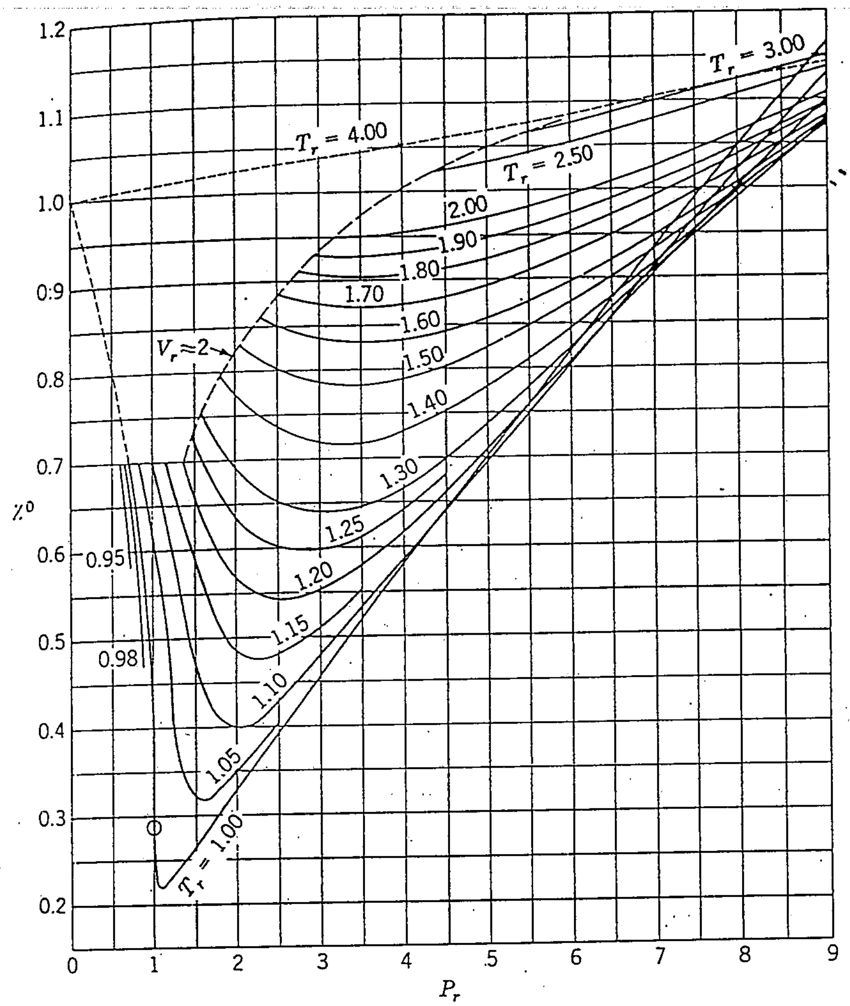

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SUBJECT 7-34 #1

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$P = \sum p_i = \sum_i p_i^o x_i$ Assuming ideal gas, ideal liquid!

a) 1) $3000 = x_e(14000) + x_p(2700) + x_B(500)$

2) $x_e + x_p + x_b = 1$

3) $x_p = x_b$

Solve 3 eq'ns, 3 unknowns

$3000 = x_e\, 14000 + 3200\, x_p$

$x_e + 2x_p = 1, \quad x_e = 1 - 2x_p$

$3000 = 14000(1-2x_p) + 3200\, x_p$

$$\boxed{\begin{aligned} x_p &= 0.4436 \\ x_b &= 0.4436 \\ x_e &= 0.1128 \end{aligned}}$$

b) $y_i = \frac{x_i P_i^o}{P}$

$$\boxed{\begin{aligned} y_e &= \frac{(0.1128)(14000)}{3000} = 0.5264 \\ y_p &= \frac{(0.4436)(2700)}{3000} = 0.3992 \\ y_b &= \frac{(0.4436)(500)}{3000} = 0.0739 \end{aligned}}$$

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SUBJECT 7-35 #1

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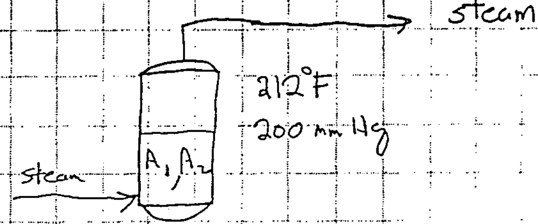

$P^\circ_{A_1} = 32$ mm Hg

$P^\circ_{A_2} = 14$ mm Hg

How many lbs of steam required per mole acid recovered?

Raoult's Law: $x_{A_1} P^\circ_{A_1} + x_{A_2} P^\circ_{A_2} + P_{H_2O} = 200$ (1)

water is superheated steam immiscible with acids

$$x_{A_1} + x_{A_2} = 1$$

$$Y_{A_1} = \frac{x_{A_1} P^\circ_{A_1}}{P} \qquad Y_{A_2} = \frac{x_{A_2} P^\circ_{A_2}}{P}$$

Given $x_{A_1} = x_{A_2} = 0.5$

By (1) $(0.5)(32) + (0.5)(14) + P_{H_2O} = 200$ mm Hg

$$P_{H_2O} = 177 \text{ mm Hg}$$

$$y_{H_2O} = P_{H_2O}/P = 177/200 = 0.885$$

$$\frac{\text{lb } H_2O}{\text{mole acid}} = \left(\frac{0.885 \text{ mol } H_2O}{\text{mol vapor}}\right)\left(\frac{\text{mol vapor}}{(1-0.885)\text{ mol acid}}\right)\left(\frac{18 \text{ lb } H_2O}{\text{mol } H_2O}\right) = \boxed{138.5 \frac{\text{lb } H_2O}{\text{mol acid}}}$$

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SUBJECT 7-35 #6

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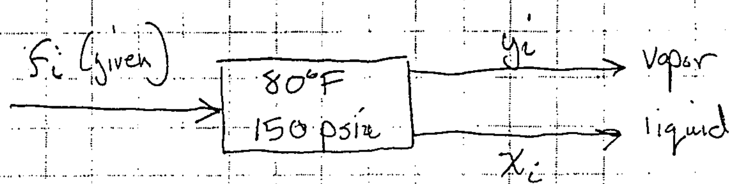

$V = L = 0.5$

$y_i = K_i x_i$

Overall Balance: $F = V + L$

Component Balance: $f_i = v_i + l_i$

$f_i = y_i V + x_i L$

$f_i = K_i x_i V + x_i L = x_i(K_i V + L)$

$x_i = f_i / (K_i V + L)$

This problem is over-specified! (Normally, the fraction vaporized would be unknown! It would be T + E so that the V would be changed so that $(\Sigma x_i)_{calc} = 1$

i	f_i (given)	K_i (given)	$x_i = f_i / (K_i V + L)$
CH_4	0.1	17	0.0111
C_2H_6	0.2	3.1	0.0976
C_3H_8	0.3	1.0	0.3000
$i\text{-}C_4H_{10}$	0.15	0.44	0.2083
C_4H_{10}	0.2	0.32	0.3030
C_5H_{12}	0.05	0.0986	0.0910
			1.011

← $V \neq 0.5$ or else this would be 1!

Bonus VLE Question:

A mixture of 70 mole % n-butane, 4 mole % water, and 26 mole % nitrogen is at 75°C and 50 psia. Antoine constants are given below:

Form: $\log_{10}P^{sat} = A - B/(T + C)$
where T is the temperature in °C
Psat is the vapor pressure in mmHg

Compound	A	B	C
n-butane	6.85353	955.43	241.0
water	8.10765	1750.286	235.0

1. Liquid mixtures of butane and water can be characterized as:
   A. ideal
   B. non-ideal
   C. highly non-ideal
   D. cannot be characterized

2. At 50 psia, as the temperature is reduced, which of the following observations best describes the essential nature of the problem?
   A. high boilers condense first
   B. low boilers condense first
   C. there exists a dew point
   D. there exist multiple dew points

3. At what temperature will the first drop of liquid form?
   A. 32°C
   B. 35°C
   C. 49°C
   D. 52°C

4. The composition of the first drop of liquid will be:
   A. water
   B. butane
   C. nitrogen
   D. 70% butane, 4% water, 26% nitrogen

5. At 50 psia, essentially no butane will condense until the temperature is reduced below:
   A. 0°C
   B. 26°C
   C. 32°C
   D. 52°C

Answers:

1. C. The butane / water system is extremely non-ideal. In fact, they are essentially immiscible and form two liquid phases.

2. D. Because nitrogen is above its critical temperature, it is essentially non-condensible. Also, butane and water can be considered to be immiscible liquids. Therefore, there will be two dew points. The first will be water condensing and the second will be butane.

Raoults' law: $P = P_w + P_b + P_n$
but $P_w = y_wP = x_wP_w^{sat} = P_w^{sat}$ since a separate water liquid phase will form
$P_b = y_bP = x_bP_b^{sat} = P_b^{sat}$ since a separate butane liquid phase will form

3. D. As shown above, liquid water will be in equilibrium with water in the vapor when $P_w = P_w^{sat}$. The partial pressure of water is (0.04)(50 psia) = 2 psi or 103 mmHg. Trial and error using the Antoine equation shows that the vapor pressure of water will be 103 mmHg at 52°C. This water dew point is higher than the butane dew point calculated below.

4. A. see 3.

5. B. Since water is condensing, the partial pressure of butane will change, but a first guess is that 1 mole% water is left in the vapor leaving 73 % butane. The butane partial pressure would then be (0.73)(50 psia) =36.5 psi or 1888 mmHg. Trial and error using the Antoine equation shows that the vapor pressure of butane will be 1888 mmHg at 26°C. At this temperature, the vapor pressure of water is 25 mmHg, so that the vapor mole fraction of water is about 0.014 which is close to our assumption.