University Of Jordan

Faculty of Engineering and Technology
Department of Chemical Engineering

Chemical Engineering Principles 2
(0905212)

Mixing and Solutions

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Introduction

- In certain case, upon mixing two liquids (such as concentrated sulfuric acid and water) or dissolving a solid in a liquid (such as sodium hydroxide in water), the mixture or solution became quite hot.
- When two different liquids are mixed or when a gas or solid is dissolved in a liquid,
  - Bonds are broken between neighboring molecules-and possibly between atoms--of the feed materials, and
  - New bonds are formed between neighboring molecules or ions in the product solution.
  - If less energy is required to break the bonds in the feed materials than is released when the solution bonds form, a net release of energy results.
  - Unless this energy is transferred from the solution to its surroundings as heat, it goes into raising the solution temperature
- The **heat of solution** at a given temperature and pressure is the difference between the enthalpy of the solution at the specified temperature and pressure and the total enthalpy of the pure solute and solvent at the same T and P.

The heat of solution

- If 1 mol of pure liquid sulfuric acid mixed with water at a specified temperature and pressure, temperature rise occurs.
- If the mixture is then cooled at constant pressure to bring it back to the initial temperature. Then, the energy balance for this constant-pressure process is

$$Q = \Delta H = H_{H_2SO_4(aq)} - (H_{H_2SO_4(l)} + H_{H_2O})$$

And ΔH is the heat of solution

- An **ideal mixture** is one for which the heat of mixing or solution is negligible

$$H_{\text{mixture}} \approx \sum n_i \hat{H}_i,$$

where n_i is the amount of mixture component i and $\hat{H}_i$ is the specific en

The heat of solution and mixing

The **heat of solution** $\Delta\hat{H}_s(T,r)$ is defined as the change in enthalpy for a process in which 1 mole of a solute (gas or solid) is dissolved in r moles of a liquid solvent at a constant temperature T.

- As r becomes large, $\Delta\hat{H}_s$ approaches a limiting value known as the heat of solution at infinite dilution.
- The heat of mixing has the same meaning as the heat of solution when the process involves mixing two fluids rather than dissolving a gas or solid in a liquid.

Table B.11 lists values of the heats of solution at 25°C of HCl(g) and NaOH(s) in water, and the heat of mixing at 25°C of H_2SO_4(l) and water.

The heat of solution and mixing

Table B.11 Integral Heats of Solution and Mixing at 25°C

r(mol H_2O/mol solute)	$(\Delta\hat{H}_s)_{HCl(g)}$ kJ/mol HCl	$(\Delta\hat{H}_s)_{NaOH(s)}$ kJ/mol NaOH	$(\Delta\hat{H}_m)_{H_2SO_4}$ kJ/mol H_2SO_4
0.5	—	—	−15.73
1	−26.22	—	−28.07
1.5	—	—	−36.90
2	−48.82	—	−41.92
3	−56.85	−28.87	−48.99
4	−61.20	−34.43	−54.06
5	−64.05	−37.74	−58.03
10	−69.49	−42.51	−67.03
10 000	−74.99	−42.72	−87.07
50 000	−75.08	−42.80	—
100 000	−75.10	—	−93.64
500 000	—	—	−95.31
∞	−75.14	−42.89	−96.19

The heat of solution and mixing

Example

calculate ΔH for a process in which 2 mol of potassium cyanide (KCN) is dissolved in 400 mol of water at 18°C.

- The enthalpy of a solution containing r moles H_2O/mole solute is for reference states of pure solute and solvent at 25°C and 1 atm. $\hat{H} = \Delta \hat{H}_s(r)$
- The enthalpy of a solution for reference states of pure solvent and an infinitely dilute solution at 25°C and 1 atm $\hat{H} = \Delta \hat{H}_s(r) - \Delta \hat{H}_s(\infty)$

The heat of solution and mixing

Example

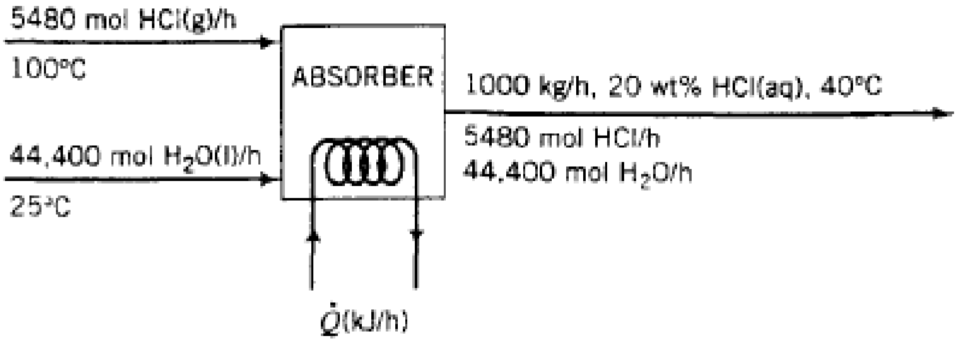
Calculate ΔH for a hydrochloric acid solution for which r = 10 moles H_2O/mole HCl.

The heat of solution and mixing

Balances on Dissolution and Mixing Processes

Example ***Production of Hydrochloric Acid***

Hydrochloric acid is produced by absorbing gaseous HCl (hydrogen chloride) in water. Calculate the heat that must be transferred to or from an absorption unit if HCl(g) at 100°C and $H_2O(l)$ at 25°C are fed to produce 1000 kg/h of 20.0 wt% HCl(aq) at 40°C.



Example Cont.

Enthalpy-Concentration Charts-Single Liquid Phase

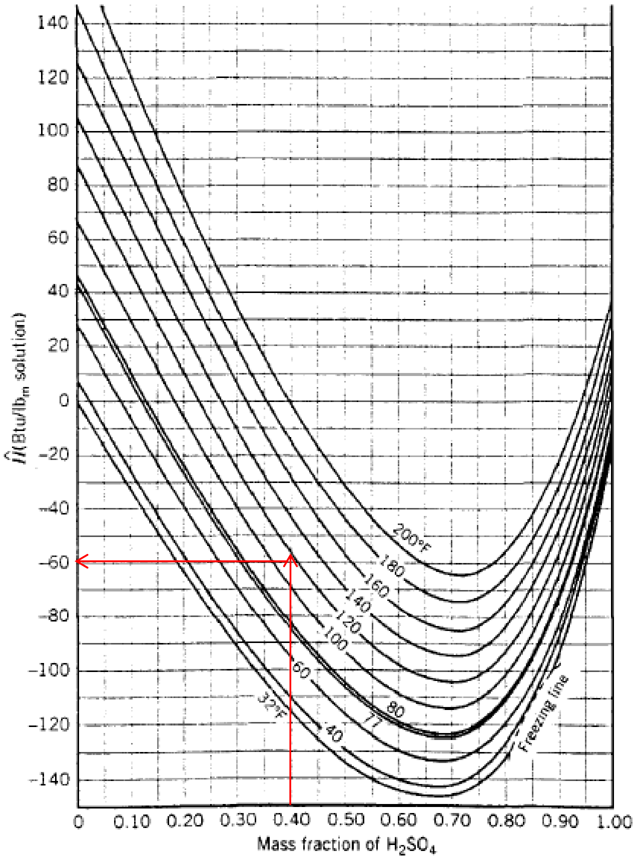
- **Enthalpy-concentration chart, a plot of specific enthalpy** versus mole fraction (or mole percent) or mass fraction (or weight percent) of one component in binary (two component) systems.

Enthalpy–concentration chart for H_2SO_4–H_2O

- The reference conditions for the plotted enthalpies are pure liquid H_2SO_4 at 77°F and liquid water at 32°F.

Example

Calculate the specific enthalpy (Btu/Ibm) of a 40 wt% sulfuric acid solution at 120°F.



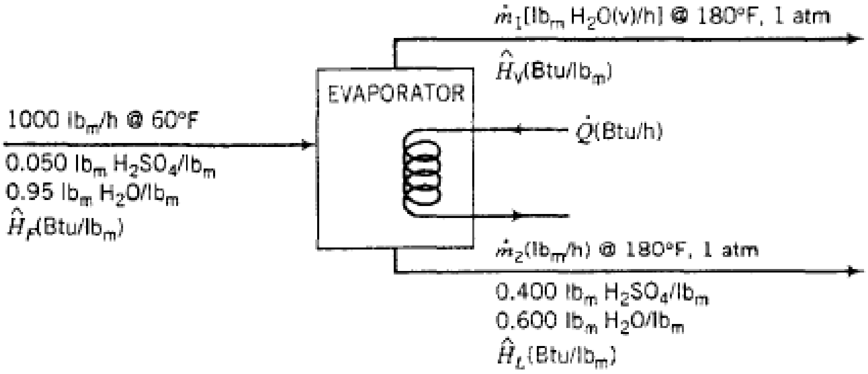
Example Cont.

Example Cont.

Example Cont.

Example *Concentration of an Aqueous H_2SO_4 Solution*

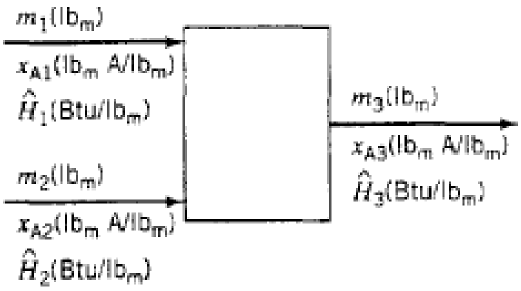
A 5.0 wt% H_2SO_4 solution at 60°F is to be concentrated to 40.0 wt% by evaporation of water. The concentrated solution and water vapor emerge from the evaporator at 180°F and 1 atm. Calculate the rate at which heat must be transferred to the evaporator to process 1000 lb_m/h of the feed solution.



Adiabatic mixing

Adiabatic mixing processes are particularly simple to analyze when an $\hat{H}$-x chart is available.

Suppose x_A is the mass fraction of A in a mixture of two species. A and B, and that a mass m_1 of Solution 1 $(x_{A1}, \hat{H}_1)$ is mixed adiabatically with a mass m_2 of Solution 2 $(x_{A2}, \hat{H}_2)$.



Total Mass Balance: $m_1 + m_2 = m_3$

A Balance: $m_1 x_{A1} + m_2 x_{A2} = m_3 x_{A3}$

$$\Rightarrow \quad m_1(x_{A3} - x_{A1}) = m_2(x_{A2} - x_{A3})$$

Energy Balance: $\Delta H = m_3\hat{H}_3 - m_1\hat{H}_1 - m_2\hat{H}_2 = 0$

$$\Rightarrow \quad m_1(\hat{H}_3 - \hat{H}_1) = m_2(\hat{H}_2 - \hat{H}_3)$$

Dividing

$$\Rightarrow \quad \frac{\hat{H}_3 - \hat{H}_1}{x_{A3} - x_{A1}} = \frac{\hat{H}_2 - \hat{H}_3}{x_{A2} - x_{A3}}$$

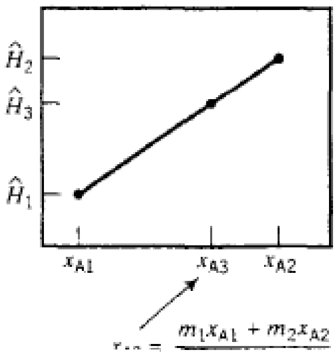
Adiabatic mixing

Since the slope of the line segment from $(x_{A1}, \hat{H}_1)$ to $(x_{A3}, \hat{H}_3)$ (the left-hand side of this equation) equals the slope of the segment from $(x_{A3}, \hat{H}_3)$ to $(x_{A2}, \hat{H}_2)$ (the right-hand side) and the segments have a point in common, the three points must lie on a straight line.

The value of x_{A3}

$$x_{A3} = \frac{m_1 x_{A1} + m_2 x_{A2}}{m_1 + m_2}$$

the product mixture, $(x_{A3}, \hat{H}_3)$, is on a straight line on the $\hat{H}$-x chart between the points corresponding to the feed stream conditions.



It follows that

if two feed solutions of known masses and compositions $(m_i, x_i, i = 1, 2)$ are mixed adiabatically and you have an $\hat{H}$-x chart,

(i) calculate x_3 for the product mixture

ii. draw a line connecting the points on the chart corresponding to the two feeds,

iii. read the enthalpy and temperature of the product mixture from the point on the connecting line for which $x = x_3$.

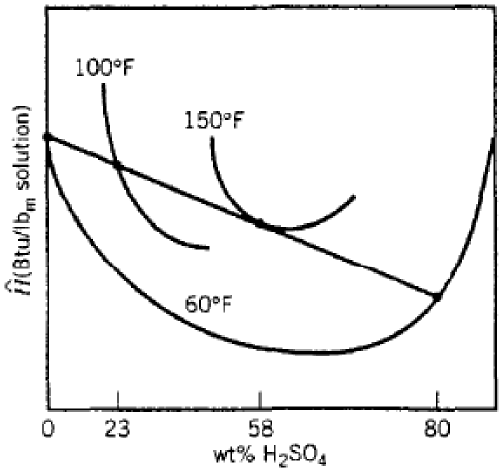
Adiabatic mixing

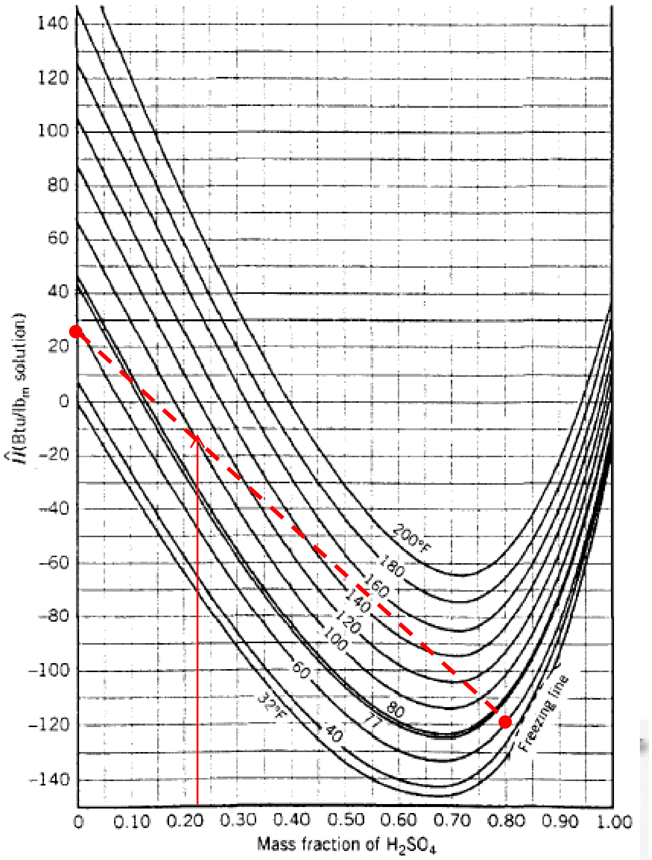
Example

Pure water at 60°F is mixed with 100 g of an aqueous 80 wt% H_2SO_4 solution, also at 60°F. The mixing vessel is insulated well enough to be considered adiabatic.

1. If 250 g H_2O is mixed with the acid, what will the final solution temperature be?
2. What is the maximum attainable solution temperature and how much water must be added to achieve it?

Example Cont.





Using Enthalpy-Concentration Charts for Vapor-Liquid Equilibrium Calculations

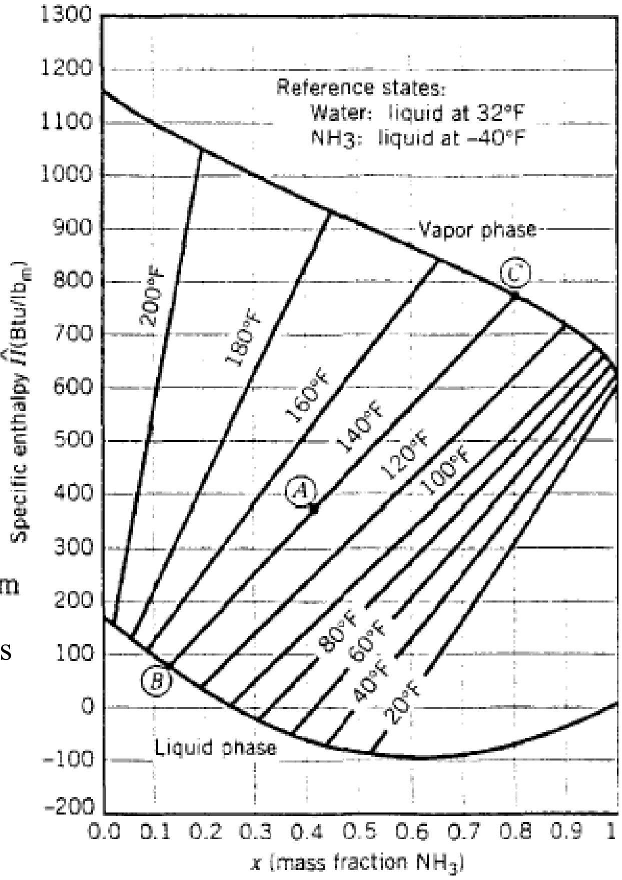
- Enthalpy-concentration charts are particularly useful for two-component systems in which vapor and liquid phases are in equilibrium

DF = (2 + 2 − 2) = 2 degrees of freedom.

- If as before we fix the system pressure, then
  - specifying only one more intensive variable-the system temperature, or the mass or mole fraction of either component in either phase- fixes the values of all other intensive variables in both phases.

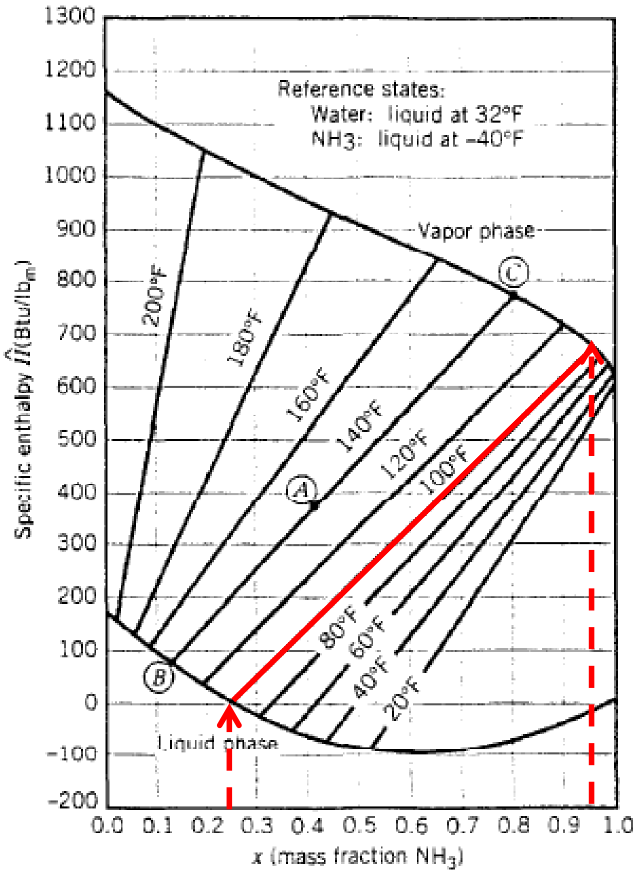
$\hat{H}$-x diagram for the ammonia–water system at 1 atm

- In this diagram, the specific enthalpies of aqueous solutions and gaseous mixtures of ammonia and water are presented



Using Enthalpy-Concentration Charts for Vapor-Liquid Equilibrium Calculations

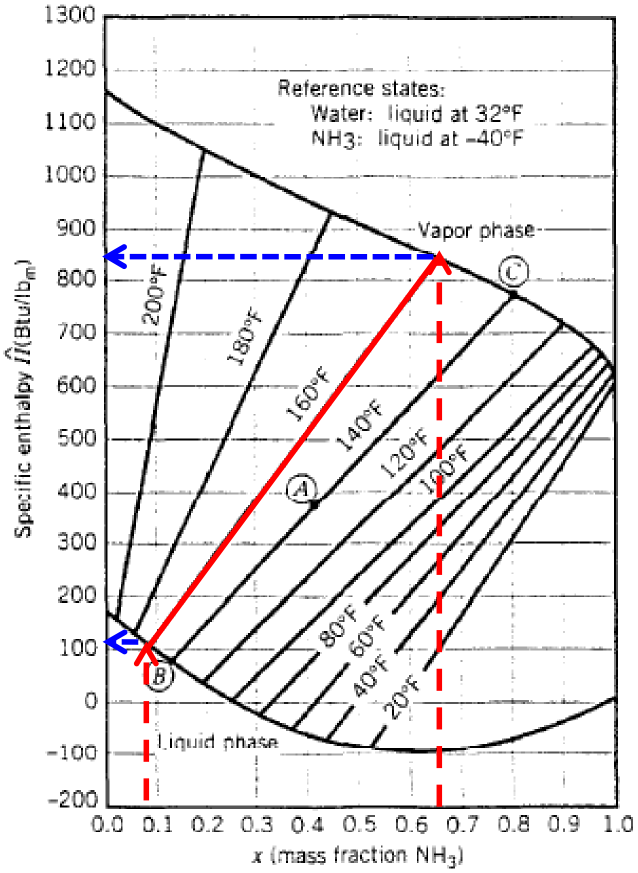
- If the mass fraction of ammonia in a liquid solution of NH_3 and H_2O at 1 atm is specified to be 0.25, then
- The system temperature and the mass fraction of NH_3 in the vapor phase are uniquely determined by these specifications
- A tie line is drawn on the enthalpy-concentration chart from $x = 0.25$ on the liquid phase curve to the corresponding point on the vapor-phase curve, which is at $y = 0.95$.
- Tie line may be labeled with the corresponding temperature, 100°F.



Example

Use of the Enthalpy-Concentration Chart for a Two-Phase System

An aqueous ammonia solution is in equilibrium with a vapor phase in a closed system at 160°F and 1 atm. The liquid phase accounts for 95% of the total mass of the system contents. Determine the weight percent of NH_3 in each phase and the enthalpy of the system per unit mass of the system contents.



Example Cont.

- If the overall composition of a two-phase two-component system at a given temperature and pressure is known, the fraction of the system that is liquid or vapor may easily be determined from the enthalpy concentration chart.

Example

A mixture of ammonia and water that is 40% NH_3 by mass is contained in a closed vessel at 140°F and 1 atm. Find the L/V ratio.

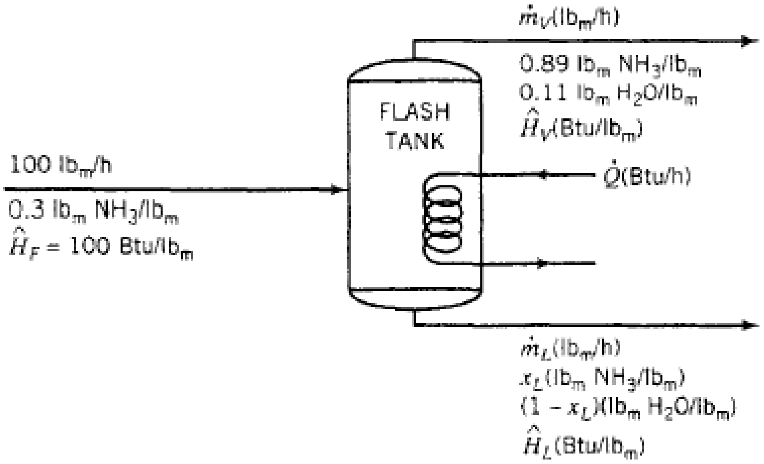
Example Cont.

Example Cont.

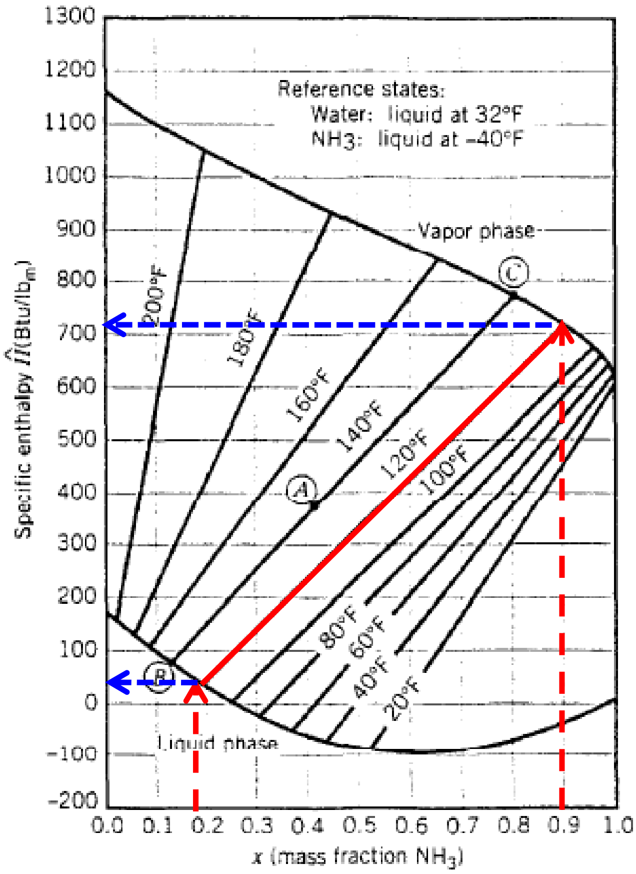
Example

Equilibrium Flash Vaporization

A 30 wt% NH_3 solution at 100 psia is fed at a rate of 100 lb_m/h to a tank in which the pressure is 1 atm. The enthalpy of the feed solution relative to the reference conditions used to construct Figure 8.5-2 is 100 Btu/lb_m. The vapor composition is to be 89 wt% NH_3. Determine the temperature of the stream leaving the tank, the mass fraction of NH_3 in the liquid product, the flow rates of the liquid and vapor product streams, and the rate at which heat must be transferred to the vaporizer.



Example Cont.



Example Cont.