CHAPTER 13

Heats of Solution and Mixing

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13.2 Introducing the Effects of Mixing into the Energy Balance 715

Your objectives in studying this chapter are to be able to

1. Distinguish between ideal solutions and real solutions
2. Understand how energy changes occur on mixing
3. Distinguish between integral heat of solution, differential heat of solution, heat of solution at infinite dilution, and heat of solution in the standard state
4. Calculate the heat of mixing, or the heat of dissolution, at standard conditions given the moles of the materials forming the mixture and experimental data
5. Calculate the standard integral heat of solution
6. Apply an energy balance to problems in which the heat of mixing is significant
7. Use an enthalpy-concentration chart in solving material and energy balances

We have deferred consideration of the heat of solution/mixing until this chapter to avoid making the presentation of energy balances more complicated. But, in many processes, the energy involved when solution/mixing occurs is too large to be ignored. Recall from chemistry the warning "Never add water to sulfuric acid, but slowly add the acid to water."

Looking Ahead

In this chapter we explain how mixing and solution of one component in another to form a binary solution affect the energy balance. We focus only on binary mixtures here. You will learn several new terms and related calculations that affect the enthalpy terms in the general energy balance.

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13.1 Heats of Solution, Dissolution, and Mixing

Up to this chapter we have assumed that when a stream consists of several components, the total properties of the stream are the appropriately weighted sum of the properties of the individual components. For such **ideal solutions,** we could write down for the heat capacity of an ideal mixture, for example,

$$C_{p\,\text{mixture}} = x_A C_{p_A} + x_B C_{p_B} + x_C C_{p_C} + \cdots$$

or, for the enthalpy,

$$\Delta\hat{H}_{\text{mixture}} = x_A \Delta\hat{H}_A + x_B \Delta\hat{H}_B + x_C \Delta\hat{H}_C + \cdots$$

In particular, mixtures of gases have been treated as ideal solutions.

However, you must take into consideration other types of mixtures. You can prepare various kinds of binary solutions or mixtures:

a. gas-gas
b. gas-liquid
c. gas-solid
d. liquid-liquid
e. liquid-solid
f. solid-solid

You can ignore the energy changes that occur on mixing for cases a, c, and f. They are negligible. The other mixtures constitute **real solutions.** When a gaseous or solid **solute** (the compound to be dissolved) is mixed with a liquid **solvent** (the compound in which the solute is dissolved), the energy effect that occurs is referred to as the **heat** (really **enthalpy**) **of solution.** When a liquid is mixed with a liquid, the energy effect is called the **heat (enthalpy) of mixing.** The negative of the heat of solution or mixing is the **heat (enthalpy) of dissolution.**

The heat of solution can be positive (endothermic) or negative (exothermic). Examine Figure 13.1, which shows the relative enthalpy values of a mixture of a fluorocarbon (C_6F_6) in benzene (C_6H_6).

You can treat heats of solution/mixing in the same way you treat chemical reactions. In the energy balance, you can (a) merge the heats of solution/mixing of the compounds in the system with the heats of formation, or (b) consolidate the effects of the heats of solution/mixing in one lumped term analogous to a heat of reaction term. For example, let us represent the solution of 1 g mol of HCl(g) into 5 g mol of $H_2O(l)$ by the following chemical equation:

$$HCl(g) + 5H_2O(l) \rightarrow HCl[5H_2O]$$

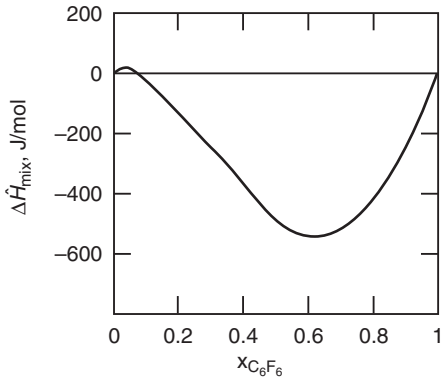


Figure 13.1 Relative enthalpy change on mixing C_6F_6 in C_6H_6 at 25°C

If you carry out experiments to measure the heat transfer from an apparatus at a constant 25°C and 1 atm by successively adding water to HCl, and arrange the experiments so that the energy balance reduces to $Q = \Delta H$, then the values of ΔH would be the tabulation in the third column of Table 13.1. (The values incorporate a slight adjustment in the measured values of Q at the vapor pressure of the solution to adjust them to 1 atm, the standard state.) If you cumulate each incremental change in ΔH, you would obtain the fourth column in Table 13.1. Appendix I on the CD that accompanies this book contains other tables listing the heats of solution for common compounds. Table 13.1 shows that there are actually two concepts that incorporate the name "heat of solution":

a. The **incremental (differential) heat of solution,** column 3
b. The **integral heat of solution,** column 4—the heat of solution for the combination of 1 mole of HCl(g) with n moles of $H_2O(l)$

Usually "heat of solution" refers to concept b, and **the enthalpy change is stated per mole of solute.**

Figure 13.2 is a plot of the values listed in column 4 of Table 13.1. The asymptotic value of the heat of solution of HCl dissolved in an infinite amount of water is known as the **heat of solution at infinite dilution** (−75, 144 J/g mol HCl).

If you want to calculate the heat of formation of any of the solutions of HCl(g) in $H_2O(l)$, all you have to do is add the heat of solution to the heat of formation of HCl(g), as shown in column 5 in Table 13.1

$$\Delta\hat{H}^{o}_{f,solution} = \Delta\hat{H}^{o}_{f,solute} + \Delta\hat{H}^{o}_{solution} \tag{13.1}$$

where $\Delta\hat{H}^{o}_{solution}$ is the integral heat of solution at standard conditions per mole of HCl, and $\Delta\hat{H}^{o}_{f,solution}$ is the heat of formation of the solution itself per

Table 13.1 Heat of Solution Data at 25°C and 1 atm

Composition	Total Moles H_2O Added to 1 mole HCl	$\Delta\hat{H}^o$ for Each Incremental Step (J/g mol HCl)	Integral Heat of Solution (Cumulative $\Delta\hat{H}^o$) (J/g mol HCl)	Heat of Formation $\Delta\hat{H}_f^o$ (J/g mol HCl)
HCl(g)	0			−92,311
HCl[1H_2O(aq)]	1	−26,225	−26,225	−118,536
HCl[2H_2O(aq)]	2	−22,593	−48,818	−141,129
HCl[3H_2O(aq)]	3	−8033	−56,851	−149,161
HCl[4H_2O(aq)]	4	−4351	−61,202	−153,513
HCl[5H_2O(aq)]	5	−2845	−64,047	−156,358
HCl[8H_2O(aq)]	8	−4184	−68,231	−160,542
HCl[10H_2O(aq)]	10	−1255	−69,486	−161,797
HCl[15H_2O(aq)]	15	−1503	−70,989	−163,300
HCl[25H_2O(aq)]	25	−1276	−72,265	−164,576
HCl[50H_2O(aq)]	50	−1013	−73,278	−165,589
HCl[100H_2O(aq)]	100	−569	−73,847	−166,158
HCl[200H_2O(aq)]	200	−356	−74,203	−166,514
HCl[500H_2O(aq)]	500	−318	−74,521	−166,832
HCl[1000H_2O(aq)]	1000	−163	−74,684	−166,995
HCl[50,000H_2O(aq)]	50,000	−146	−75,077	−167,388
HCl[∞H_2O]		−67	−75,144	−167,455

SOURCE: *National Bureau of Standards Circular 500,* U.S. Government Printing Office, Washington, DC (1952).

mole of HCl. It is important to remember that **the heat of formation of the H_2O does not enter into the calculation** in Equation (13.1); it is defined as zero for the process of solution. Tables in reference books usually list data for the heats of formation of solutions in the standard state rather than the heats of solution themselves. In the following processes and examples, we assume that the systems are open, steady-state, or, if closed, that the accumulation term in the energy balance is $\Delta U = \Delta H$ so that we discuss only enthalpies.

You can treat a solution as a single compound in making calculations in an energy balance by using the property that enthalpies of solutions are state variables. One convenient procedure is to merge the heats of solution of a compound with the heats of formation, as indicated in column 5 of Table 13.1

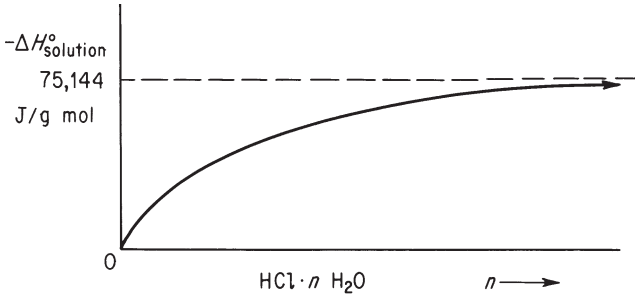


Figure 13.2 Integral heat of solution of HCl in water

and by Equation (13.1). Then the specific enthalpy of a solution relative to S.C. would be

$$\hat{H}_{\text{solution}}(T) = \Delta\hat{H}^{\circ}_{\text{f,solution}} + [\hat{H}(T) - \hat{H}(\text{S.C.})]_{\text{solution}} \qquad (13.2)$$

where the term in the brackets represents the sensible heat of the solution itself (any phase change is unlikely).

For example, suppose you want to find the $\Delta\hat{H}^{\circ}_{\text{solution}}$ that occurs at S.C. when a solution of 1 g mol of HCl dissolved in 1 g mol of H_2O is placed in an infinite amount of water. Use the data listed in column 5 of Table 13.1, and subtract the enthalpy of the initial state from the enthalpy of the final state as follows:

$$(-167{,}455) - (-118{,}536) = -48{,}911 \text{ J/g mol HCl}$$

As another example, consider a process in which a dilute solution of HCl is to be concentrated. Because enthalpy changes for heats of solution are state variables, you can easily look up the heats of formation of HCl solutions at their respective concentrations. Then you can calculate the enthalpy change between the final and initial states for a closed process, or the enthalpy change between the output and the input for a flow process. Thus, if you mix 1 mole of HCl[$15H_2O$] and 1 mole of HCl[$5H_2O$], you obtain 2 moles of HCl[$10H_2O$], and the total enthalpy change at 25°C and 1 atm is

$$\begin{aligned}\Delta H^{\circ} &= [2(-69{,}486)] - [1(-70{,}989) + 1(-64{,}047)] \\ &= -3936 \text{ J}\end{aligned}$$

You would have to remove 3936 J to keep the temperature of the final mixture at 25°C.

We should mention that the solution of a hydrated salt such as $CaCl_2 \cdot 6H_2O$ requires a little care in the calculations. If you mix the hydrated salt with water or a $CaCl_2$ solution, the procedure to calculate the enthalpy change is as follows: You first have to decompose (melt) the hydrated salt into a solid and water. Then you dissolve the total salt available into the total water available after the melting and solution. For example, from the data in problem 13.3, if 1 g mol of $Na_2CO_3 \cdot 7H_2O$ is dissolved in 8 g mol of $H_2O(l)$, the resulting solution contains 1 g mol of Na_2CO_3 and 15 g mol of H_2O. The melting step involves the following enthalpy change:

	$Na_2CO_3 \cdot 7H_2O(s)$	$\rightarrow$	$Na_2CO_3(s)$	+	$7H_2O(l)$
$\Delta\hat{H}^{\circ}_f$(kJ/g mol):	−3201.18		−1130.92		−285.840

$$\Delta H^{\circ} = [7(-285.840) + 1(-1130.92)] - [1(-3201.18)] = +69.38 \text{ kJ}$$

The solution step is

$$\begin{array}{lccc} & Na_2CO_3(s) & + \quad 15\,H_2O(l) & \rightarrow \quad Na_2CO_3[15H_2O] \\ \Delta\hat{H}_f^o(\text{kJ/g mol}): & -1130.92 & 0 & -1163.70 \end{array}$$

$$\Delta H^o = (-1163.70) - (-1130.92) = -32.78 \text{ kJ}$$

The overall enthalpy change is 69.38 −32.78 = 36.60 kJ.

Example 13.1 Application of Heat of Solution Data

You are asked to prepare an ammonium hydroxide solution at 77°F by dissolving gaseous NH_3 in water. Calculate (a) the amount of cooling needed in British thermal units to prepare a 3.0% solution containing 1 lb mol of NH_3, and (b) the amount of cooling needed in British thermal units to prepare 100 gal of a solution of 32.0% NH_3.

Data: The following heat of solution data have been taken from *NBS circular 500.*

Composition	State	$-\Delta\hat{H}_f^o$ (Btu/lb mol)	$-\Delta\hat{H}_{soln}^o$ (Btu/lb mol)
	g	19,900	0
$1H_2O$	aq	32,600	12,700
$2H_2O$	aq	33,600	13,700
$3H_2O$	aq	34,000	14,100
$4H_2O$	aq	34,200	14,300
$5H_2O$	aq	34,350	14,450
$10H_2O$	aq	34,600	14,700
$20H_2O$	aq	34,700	14,800
$30H_2O$	aq	34,700	14,800
$40H_2O$	aq	34,700	14,800
$50H_2O$	aq	34,750	14,850
$100H_2O$	aq	34,750	14,850
$200H_2O$	aq	34,800	14,900
$\infty\ H_2O$	aq	34,800	14,900

Solution

The solution will be presented in abbreviated form.
Reference temperature: 77°F

a. Basis: 1 lb mol $NH_3 \equiv 17$ lb NH_3

$$\text{wt \% } NH_3 = \frac{\text{lb } NH_3}{\text{lb } H_2O + \text{lb } NH_3}\,(100)$$

$$3 = \frac{17(100)}{17 + m_{H_2O}} \qquad m_{H_2O} = 550 \text{ lb or about } 30 \text{ lb mol } H_2O$$

(*Continues*)

Example 13.1 Application of Heat of Solution Data (*Continued*)

From the table above, the $\Delta\hat{H}^{o}_{soln} = -14{,}800$ Btu/lb mol NH_3, which is equal to 14,800 Btu removed from the system.

b. Basis: 100 gal solution

From Lange's *Handbook of Chemistry*, a 32.0% solution of NH_3 has the following properties:

	NH_3	H_2O
Sp.gr.:	0.889	1.003

The density of the 32.0% solution in pounds per 100 gal is

$$\frac{(0.889)(62.4)(1.003)(100)}{7.48} = 744 \text{ lb}/100 \text{ gal}$$

$$\frac{744(0.32)}{17} = 14.0 \text{ lb mol } NH_3/100 \text{ gal solution}$$

Basis: 1 lb mol NH_3

$$32.0 = \frac{1700}{17 + m_{H_2O}} \qquad m_{H_2O} = 36 \text{ lb and } n_{H_2O} = 2 \text{ lb mol}$$

$$\left.\begin{matrix}\text{Cooling req'd}\\ \text{Btu/100 gal}\end{matrix}\right\} = \left(\frac{\text{lb mol } NH_3}{100 \text{ gal}}\right)\left(-\Delta H^{o}_{soln}\frac{\text{Btu}}{\text{lb mol } NH_3}\right)$$

$$\left.\begin{matrix}\text{Cooling req'd}\\ \text{for 100 gal}\\ \text{32.0\% } NH_3 \text{ soln}\end{matrix}\right\} = (14.0)(-13{,}700) = -191{,}000 \text{ Btu}/100 \text{ gal soln (heat removed)}$$

Self-Assessment Test

Questions

1. Define and show on a sketch (a) the integral heat of solution, and (b) the differential heat of solution.
2. Indicate whether the following statements are true or false:
   a. Heats of reaction and heats of solution represent the same physical phenomena.
   b. All mixtures have significant heats of solution.
   c. The heat of mixing at infinite dilution involves an infinite amount of solvent.
   d. Heats of solution can be positive and negative.
   e. A gas mixture is usually an ideal solution.
3. a. What is the reference state for H_2O in the table for the heat of solution of HCl?
   b. What is the value of the enthalpy of the H_2O in the reference state?
4. Repeat question 3 for HCl.

Problems

1. Calculate the heat of solution at standard conditions when 1 mol of a solution of 20 mol % HCl is mixed with 1 mol of a solution of 25 mol % HCl.
2. How much heat has to be added to a solution of 1 g mol of HCl in 10 g mol of H_2O to concentrate the solution to 1 g mol of HCl in 4 g mol of H_2O?
3. The heat of formation of H_2SO_4 is -811.319 kJ/g mol H_2SO_4. What is the heat of formation per gram mole of H_2SO_4 of a solution of 20% sulfuric acid?

Thought Problems

1. A tanker truck of hydrochloric acid was inadvertently unloaded into a large storage tank used for sulfuric acid. After about one-half of the 3000 gal load had been discharged, a violent explosion occurred, breaking the inlet and outlet lines and buckling the tank. What might be the cause of the explosion?
2. A concentrated solution (73%) of sodium hydroxide was stored in a vessel. Under normal operations, the solution was forced out by air pressure as needed. When application of air pressure did not work, apparently due to solidification of the caustic solution, water was poured through a manhole to dilute the caustic and free up the pressure line. An explosion took place and splashed caustic out of the manhole 15 ft into the air. What caused the incident?

Discussion Problem

A significant amount of energy is liberated when freshwater and saltwater are mixed. It has been calculated that the dilution of a cubic meter of freshwater per second in a large volume of seawater dissipates roughly 2.3 MW of power. If this energy could be put to use rather than heating the ocean, it is estimated that the potential of the flow of the Columbia River would yield 15,000 MW. The technology to collect such potential has been proposed, namely, to use a selective membrane that lets certain molecules through but holds others back. Instead of separating water from saltwater by imposing an electric potential on the membrane as in desalinization, the idea is to reverse the process and mix freshwater with saltwater to generate an electric current. The membranes are arranged so that positive ions flow in one direction and negative ions in the other direction. What do you think of the proposal?

13.2 Introducing the Effects of Mixing into the Energy Balance

In Section 13.1 we restricted the discussion and examples to the standard state (25°C and 1 atm). In this section we proceed with what happens when the temperatures of the inlet and outlet streams differ from 25°C for a binary

mixture in an open, steady-state process. (For a closed system the initial and final states of the internal energy would be involved rather than the stream flows.) You can treat problems involving the heat of solution/mixing in exactly the same way that you can treat problems involving reaction. The heat of solution/mixing is analogous to the heat of reaction in the energy balance. You can carry out the needed calculations by

a. Associating heats of formation of the compounds and solutions with each of the respective compounds and solutions, or

b. Computing the overall lumped heat of solution at the reference state,

and for either option calculating the sensible heats (and phase change effects) for the compounds and solutions from the reference state.

The next example shows the detailed procedure.

Example 13.2 Application of Heat of Solution Data

Hydrochloric acid is an important industrial chemical. To make aqueous solutions of it in a commercial grade (known as *muriatic acid*), purified HCl(g) is absorbed in water in a tantalum absorber in a steady-state continuous process. How much heat must be removed from the absorber by the cooling water per 100 kg of product if hot HCl(g) at 120°C is fed into water in the absorber as shown in Figure E13.2? The feed water can be assumed to be at 25°C, and the exit product HCl(aq) is 25% HCl (by weight) at 35°C. The cooling water does not mix with the HCl solution.

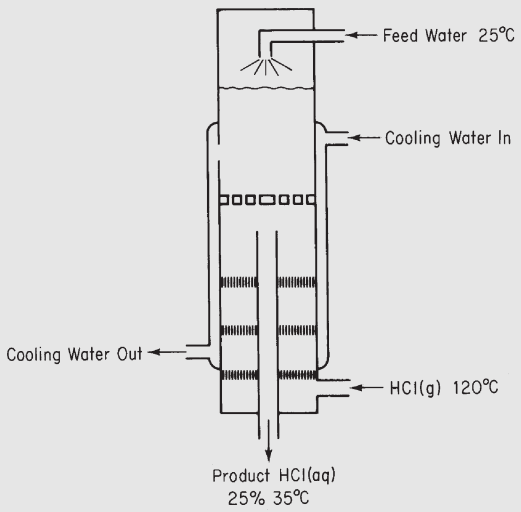


Figure E13.2

Solution

Steps 1–4

You need to convert the process data to moles of HCl to be able to use the data in Table 13.1. Consequently, we will first convert the product into moles of HCl and moles of H_2O.

Table E13.2a

Component	kg	Mol. wt.	kg mol	Mole Fraction
HCl	25	36.37	0.685	0.141
H_2O	75	18.02	4.163	0.859
Total	100		4.848	1.000

The mole ratio of H_2O to HCl is $4.163/0.685 = 6.077$.

Step 5

The system will be the HCl and water (not including the cooling water).

Basis: 100 kg of product

Ref. temperature: 25°C

Steps 6 and 7

The energy balance reduces to $Q = \Delta H$, and both the initial and final enthalpies of all of the streams are known or can be calculated directly; hence the problem has zero degrees of freedom. From simple material balances the kilograms and moles of HCl in and out, and the water in and out, are as listed in Table E13.2a above.

Step 3 (continued)

Next, you have to determine the enthalpy values for the streams. Data are: C_p for the HCl(g) is from Table G.1; C_p for the product is approximately 2.7 J/(g)(°C) equivalent to 55.6 J/(g mol) (°C); $\Delta\hat{H}_f^o$ for HCl · 6.077 $H_2O \cong -157{,}753$ J/g mol HCl. We will use $\Delta\hat{H}_f^o$ values for each stream in the calculation of ΔH.

(*Continues*)

Example 13.2 Application of Heat of Solution Data (*Continued*)

Steps 8 and 9

Table E13.2b

Stream	g mol	T(°C)	$\Delta\hat{H}_f^0$(J/g mol HCl)	$\Delta\hat{H}_{\text{sensible}}$ (J/g mol)
OUT				
HCl (aq)	4.848*	35	−157,753	$\int_{25°C}^{35°C}(2.7)\,dT$
IN				
$H_2O(\ell)$	4.163	25	−	
HCl(g)	0.685	120	−92,311	$\int_{25°C}^{120°C}(29.13-0.134\times10^{-2}\,T)\,dT$ = 2758

*HCl=0.685

$$Q = \Delta H_{\text{out}} - \Delta H_{\text{in}}$$

out *in*

$$= [0.685(-157{,}753) + 4.848(27)] - [0 + 0.685(-92{,}311) + 0.685(2758)]$$

$$= -46{,}586 \text{ J}$$

If you use heat of solution values, the calculation is (from Table 13.1 the heat of solution is −65,442 J/g mol HCl for the ratio of $HCl/H_2O = 6.077$)

$$Q = \Delta H_{\text{out, sensible}} - \Delta H_{\text{in, sensible}} + \Delta H_{\text{solution}}$$

$$= (4.848)(27) - [0.685(2753) + 0] + (0.685)(-65{,}442)$$

$$= -46{,}586 \text{ J} \quad \text{as expected}$$

In a process simulation code, table lookup or equations would be used to calculate the heats of formation at various temperatures (and pressures) other than 25°C (and 1 atm). The details would be buried in the computer code. You can better understand what the calculations for an energy balance involve if you use a graph—at the expense of some accuracy—instead of equations.

A convenient graphical way to represent enthalpy data for binary solutions is via an **enthalpy-concentration diagram.** Enthalpy-concentration diagrams (*H-x*) are plots of specific enthalpy versus concentration (usually mass or mole fraction) with temperature as a parameter. Figure 13.3 illustrates one such plot. If available,[1] such charts are useful in making combined material

[1]For a literature survey as of 1957, see Robert Lemlich, Chad Gottschlich, and Ronald Hoke, *Chem. Eng. Data Ser.*, **2**, 32 (1957). Additional references: for $CC1_4$, see M. M. Krishniah et al, *J. Chem. Eng. Data*, **10**, 117 (1965); for EtOH-EtAc, see Robert Lemlich, Chad Gottschlich, and Ronald Hoke, *Br. Chem. Eng.*, **10**, 703 (1965); for methanol-toluene, see C. A. Plank and D. E. Burke, *Hydrocarbon Process*, **45**, No. 8, 167 (1966); for acetone-isopropanol, see S. N. Balasubramanian, *Br. Chem. Eng.*, **12**, 1231 (1967); for acetonitrile-water-ethanol, see Reddy and Murti, ibid., **13**, 1443 (1968); for alcohol-aliphatics, see Reddy and Murti, ibid., **16**, 1036 (1971); and for H_2SO_4, see D. D. Huxtable and D. R. Poole, *Proc. Int. Solar Energy Soc.*, Winnipeg, August 15, 1976, **8**, 178 (1977). For more recent sources search the Internet.

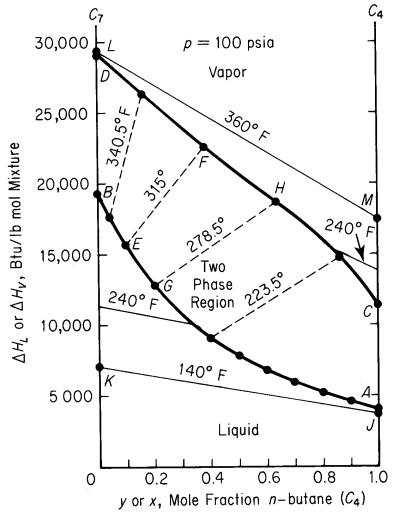


Figure 13.3 Enthalpy concentration of *n*-butane-*n*-heptane at 100 psia. Curve *DFHC* is the saturated vapor; curve *BEGA* is the saturated liquid. The dashed lines are equilibrium tie lines connecting y, the mole fraction of C_4 in the vapor, and x, the mole fraction of C_4 in the liquid, at the same temperature.

and energy balance calculations in distillation, crystallization, and all sorts of mixing and separation problems. You will find a few examples of enthalpy-concentration charts in Appendix J.

As you might expect, the preparation of an enthalpy-concentration chart requires numerous calculations and valid enthalpy or heat capacity data for solutions of various concentrations. Refer to *Unit Operations of Chemical Engineering* [W. L. McCabe and J. C. Smith, 3rd ed., McGraw-Hill, New York (1976)] for instructions if you have to prepare such a chart. In the next example we show how to use an *H-x* chart.

Example 13.3 Application of an Enthalpy-Concentration Chart

Six hundred pounds of 10% NaOH per hour at 200°F are added to 400 lb/hr of 50% NaOH at the boiling point in an insulated vessel. Calculate the following:

a. The final temperature of the exit solution
b. The final concentration of the exit solution
c. The pounds of water evaporated per hour during the process

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Solution

You can use the steam tables and the NaOH-H_2O enthalpy-concentration chart in Appendix J as your sources of data. What are the reference conditions for the chart? The reference conditions for the latter chart are $\Delta\hat{H} = 0$ at 32°F for pure liquid water, an infinitely dilute solution of NaOH. Pure caustic has an enthalpy at 68°F of 455 Btu/lb above this datum. Treat the process as a flow process even if is not. The energy balance reduces to $\Delta H = 0$. Basis: 1000 lb of final solution = 1 hr.

(*Continues*)

Example 13.3 Application of an Enthalpy-Concentration Chart (*Continued*)

You can write the following material balances:

Component	*10% solution*	+	*50% solution*	=	*Final solution*	*wt%*
NaOH	60		200		260	26
H_2O	540		200		740	74
Total	600		400		1000	100

Enthalpy data from the *H-x* chart

	10% solution	*50% solution*
$\Delta\hat{H}$(Btu/lb):	152	290

The energy balance is

10% solution		*50% solution*		*Final solution*
600(152)	+	400(290)	=	ΔH
91,200	+	116,000	=	207,200

Note that the enthalpy of the 50% solution at its boiling point is taken from the bubble point at $\omega_{NaOH} = 0.50$. The enthalpy per pound of the final solution is

$$\frac{207{,}200 \text{ Btu}}{1000 \text{ lb}} = 207 \text{ Btu/lb}$$

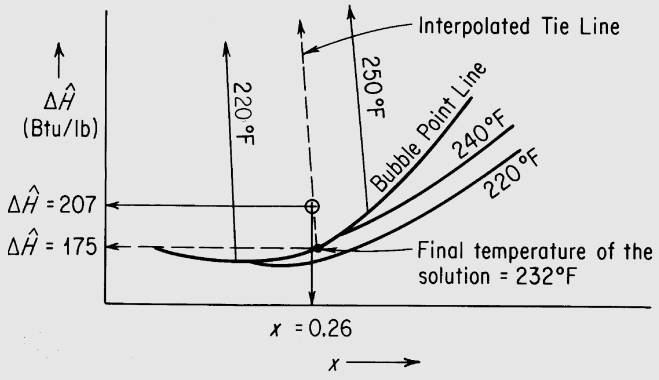


Figure E13.3

On the enthalpy-concentration chart for NaOH-H_2O, for a 26% NaOH solution with an enthalpy of 207 Btu/lb, you would find that only a two-phase mixture of (1) saturated H_2O vapor and (2) NaOH-H_2O solution at the boiling point could exist. To get the fraction H_2O vapor, you have to make an additional energy (enthalpy) balance. By interpolation, draw the tie line through the point $x = 0.26$, $H = 207$ (make it parallel to the 220°F and 250°F tie lines). The final temperature of the tie line appears from Figure E13.3 to be 232°F;

the enthalpy of the liquid at the bubble point at this temperature is about 175 Btu/lb. The enthalpy of the saturated water vapor (no NaOH is in the vapor phase) from the steam tables at 232°F is 1158 Btu/lb. Let x = pounds of H_2O evaporated.

Basis: 1000 lb of final solution

$$x(1158) + (1000 - x)\,175 = 1000\,(207.2)$$

$$x = 32.8 \text{ of } H_2O \text{ evaporated/hr}$$

Self-Assessment Test

Questions

1. Is a gas mixture an ideal solution?
2. Give **(a)** two examples of exothermic mixing of two liquids and **(b)** two examples of endothermic mixing based on your experience.
3. Indicate whether the following statements are true or false:
   a. Heat of mixing at infinite dilution involves mixing of 1 mole of solute and an infinite amount of solvent and is therefore not defined.
   b. Heats of reaction and mixing are approximately equal because they both involve molecular rearrangement.
   c. Ethyl alcohol and water form an ideal solution.
4. What are some of the significant differences between the *H-x* chart in Figure 13.3 and the integral heat of solution chart in Figure 13.2?

Problems

1. Use the heat of solution data in Appendix I to determine the heat transferred per mole of entering solution into or out of (state which) a process in which 2 g mol of a 50 mol % solution of sulfuric acid at 25°C is mixed with water at 25°C to produce a solution at 25°C containing a mole ratio of 10 H_2O to 1 H_2SO_4.
2. Calculate the heat that must be added or removed per ton of 50 wt % H_2SO_4 produced by the process shown in Figure SAT13.2P2.

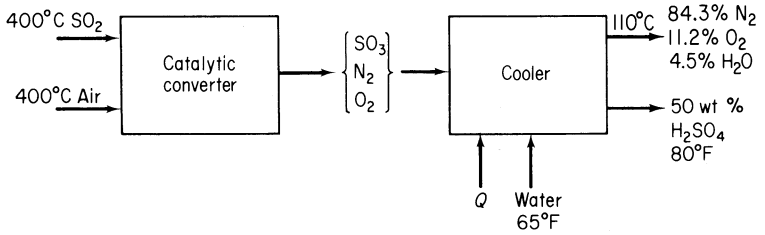


Figure SAT13.2P2

3. For the sulfuric acid–water system, what are the phase(s), composition(s), and enthalpy(ies) existing at $\Delta\hat{H} = 120$ Btu/lb and $T = 260°F$?
4. Estimate the heat of vaporization of an ethanol-water mixture at 1 atm and an ethanol mass fraction of 0.50 from the enthalpy-concentration chart in Appendix J.

Thought Problems

1. Because the driver was in a hurry, a tank truck of concentrated 6000 gal of hydrochloric acid was unloaded by mistake into a large storage tank used for concentrated sulfuric acid. After about one-half of the load had been discharged, a violent explosion took place, buckling the tank and breaking the inlet and outlet lines. What was the cause of the explosion?
2. A second example of an accident occurred in a tank as shown in Figure SAT13.2TP2. A problem occurred in discharging the NaOH (caustic) solution by air pressure because the end of the dip pipe was broken. The manhole cover was removed, and a scraper rod was lowered into the liquid to remove the broken part of the dip pipe. An immediate explosion occurred that shot NaOH solution 30 ft into the air, killing one man. What was the cause of the explosion?

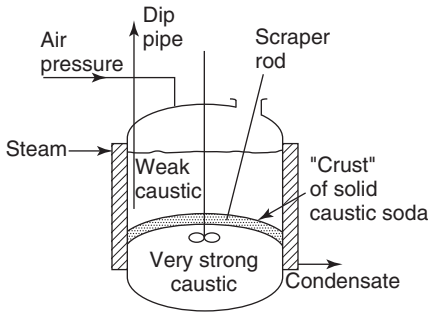


Figure SAT13.2TP2

Looking Back

In this chapter we described how to carry out energy balances when enthalpy changes occur because of the heat of solution or mixing. We also described how to use binary enthalpy-concentration charts.

Glossary

Enthalpy-concentration diagram A convenient graphical way to represent enthalpy data for binary solutions that features a plot of specific enthalpy versus concentration (usually mass or mole fraction) with temperature as a parameter.

Heat (enthalpy) of dissolution The negative of the heat of solution or mixing.

Heat (enthalpy) of mixing The enthalpy change that occurs when a liquid is mixed with a liquid.

Heat (enthalpy) of solution The enthalpy change that occurs when a solute is mixed with a solvent.

Heat of solution at infinite dilution The asymptotic value of the heat of solution of 1 mole of solute dissolved in an infinite amount of solvent.

Ideal solution A solution composed of several components in which a property is the weighted sum of the properties of the individual components.

Incremental (differential) heat of solution The derivative of the integral heat of solution curve.

Integral heat of solution The heat of solution for the combination of 1 mole of solute with n moles of solvent.

Real solution Nonideal solution.

Solute The compound that is dissolved in a solvent.

Solvent The compound in which the solute is dissolved.

Supplementary References

Berry, R. S. *Physical Chemistry,* Oxford University Press, Oxford, UK (2000).

Brandani, V., and F. Evangelista. "Correlation and Predication of Enthalpies of Mixing for Systems Containing Alcohols with UNIQUAC Associated-Solution Theory," *Ind. Eng. Chem. Res.,* **26,** 2423 (1987).

Christensen, C., J. Gmehling, and P. Rasmussen. *Heats of Mixing Data Collection,* Dechema, Frankfurt (1984).

Christensen, J. J., R. W. Hanks, and R. M. Izatt. *Handbook of Heats of Mixing,* John Wiley, New York (1982).

Dan, D., and D. P. Tassios. "Prediction of Enthalpies of Mixing with a UNIFAC Model," *Ind. Eng. Chem. Process Des. Develop.,* **25,** 22 (1986).

Johnson, J. E., and D. J. Morgan. "Graphical Techniques for Process Engineering," *Chem. Eng.,* 72 (July 8, 1985).

Sandler, S. I. *Chemical and Engineering Thermodynamics,* 3rd ed., John Wiley, New York (1998).

Smith, J. M., H. C. Van Ness, and M. M. Abbot. *Introduction to Chemical Engineering Thermodynamics,* 5th ed., McGraw-Hill, New York (1998).

Web Sites

http://www.factmonster.com/ce6/sci/A0861176.html

http://newton.dep.anl.gov/askasci/chem99/chem99198.htm

Problems

*13.1 If the heat of formation of LiCl(s) is −408.78 kJ/kg LiCl, calculate the heat of formation of LiCl in 10 mol of water. The heat of solution is −32.84 kJ/kg LiCl.

**13.2 Home ice cream makers use a mixture of 3 parts of ice to 1 part of salt (NaCl) to freeze the ice cream. Why does this process work?

Based on the following data, is salt the best compound to use (with the amount of water shown) for a freezing mixture?

Compound	$\Delta\hat{H}_f^o$(kJ/g mol)
H_2O(s)	−290.852
(l)	−285.840
(g)	−241.826
NaCl(s)	−411.00
NaCl[10H_2O]	−408.99
NH_4Cl(s)	−315.43
NH_4Cl [10H_2O]	−301.33
$CaCl_2$(s)	−794.97
$CaCl_2$ [10H_2O]	−860.03
$CaCl_2 \cdot 6H_2O$	−2586.5
$CaCl_2$ [6H_2O]	−854.4

**13.3 Based on the following data for the solution of Na_2CO_3 at S.C.:

Compound	$\Delta\hat{H}_f^o$(kJ/g mol)
Na_2CO_3(s)	−1130.92
in 15 mol H_2O	−1163.70
20	−1162.78
25	−1161.98
40	−1160.72
75	−1158.01
100	−1157.17
200	−1155.50
400	−1154.39
$Na_2CO_3 \cdot H_2O$(s)	−1430.09
$Na_2CO_3 \cdot 7H_2O$(s)	−3201.18
$Na_2CO_3 \cdot 10H_2O$(s)	−4081.9

a. Draw a standard integral heat of solution curve for sodium carbonate dissolved in water showing the heat of solution in kilojoules per mole of sodium carbonate versus mole of water.
b. If 143 kg of sodium carbonate are added to 180 kg of water, what would be the approximate final temperature of the solution if the mixing were adiabatic?

**13.4 a. From the data below, plot the enthalpy of 1 *mole of solution* at 27°C as a function of the weight percent HNO_3. Use as reference states liquid water at 0°C and liquid HNO_3 at 0°C. You can assume that C_p for H_2O is 75 J/(g mol)(°C) and for HNO_3, 125 J/(g mol)(°C).

$-\Delta H_{soln}$ at 27°C (J/g mol HNO_3)	Moles H_2O Added to 1 g mol HNO_3
0	0.0
3350	0.1
5440	0.2
6900	0.3
8370	0.5
10,880	0.67
14,230	1.0
17,150	1.5
20,290	2.0
24,060	3.0
25,940	4.0
27,820	5.0
30,540	10.0
31,170	20.0

b. Compute the energy absorbed or evolved at 27°C on making a solution of 4 moles of HNO_3 and 4 moles of water by mixing a solution of 33 1/3 mol % acid with one of 60 mol % acid.

**13.5 *National Bureau of Standards Circular 500* gives the following data for calcium chloride (mol. wt. 111) and water:

Formula	State	$-\Delta H_f$ at 25°C (kcal/g mol)
H_2O	Liquid	68.317
	Gas	57.798
$CaCl_2$	Crystal	190.0
	in 25 mol of H_2O	208.51
	50	208.86
	100	209.06
	200	209.20
	500	209.30
	1000	209.41
	5000	209.60
	∞	209.82
$CaCl_2 \cdot H_2O$	Crystal	265.1
$CaCl_2 \cdot 2H_2O$	Crystal	335.5
$CaCl_2 \cdot 4H_2O$	Crystal	480.2
$CaCl_2 \cdot 6H_2O$	Crystal	623.15

Calculate the following:

a. The energy evolved when 1 lb mol of $CaCl_2$ is made into a 20% solution at 77°F
b. The heat of hydration of $CaCl_2 \cdot 2H_2O$ to the hexahydrate
c. The energy evolved when a 20% solution containing 1 lb mol of $CaCl_2$ is diluted with water to 5% at 77°F

*13.6 For each of the following processes that occur in an open, steady-state system, calculate the heat transfer to or from the system if it is isothermal:

a. 1000 g of O_2 are mixed with 1000 g of CO_2.
b. 900 kg of water are mixed with 63 kg of nitric acid.

Data at S.C.:

Compound	$\hat{H}_f^o$ (kJ/kg)
HNO_3 (liquid)	−173.234
In 1 g mol H_2O	−186.347
$2H_2O$	−193.318
$5H_2O$	−201.962
$10H_2O$	−205.014
$50H_2O$	−205.978
$100H_2O$	−205.983

**13.7 An insulated closed tank contains 250 kg of a 20% solution of sulfuric acid at its boiling point. One hundred pounds of a 98% solution of sulfuric acid are carefully added to the original solution with stirring. What are the final temperature, composition, and weight of solution in the tank? Use Appendix J.

*13.8 An insulated tank contains 500 kg of a solution of 20% sulfuric acid at 340 K. To this solution are added 300 kg of a 96% solution of sulfuric acid at 310 K. To heat the solution, 100 kg of superheated steam are introduced at 1 atm and 400 K. What is the final temperature in the solution, and what are the concentrations of sulfuric acid and water in the final solution?

**13.9 A vessel contains 100 g of an NH_4OH-H_2O liquid mixture at 1 atm that is 15.0% by weight NH_4OH. Just enough aqueous H_2SO_4 is added to the vessel from an H_2SO_4 liquid mixture at 25°C and 1 atm (25.0 mol % H_2SO_4) so that the reaction to $(NH_4)_2SO_4$ is complete. After the reaction, the products are at 25°C and 1 atm. How much heat (in joules) is absorbed or evolved by this process? It may be assumed that the final volume of the products is equal to the sum of the volumes of the two initial mixtures.

***13.10 An ammonium hydroxide solution is to be prepared at 77°F by dissolving gaseous NH_3 in water. Prepare charts showing

a. The amount of cooling needed (in British thermal units) to prepare a solution containing 1 lb mol of NH_3 at any concentration desired
b. The amount of cooling needed (in British thermal units) to prepare 100 gal of a solution of any concentration up to 35% NH_3

If a 10.5% NH_3 solution is made up without cooling, at what temperature will the solution be after mixing?

*13.11 An evaporator at atmospheric pressure is designed to concentrate 10,000 lb/hr of a 10% NaOH solution at 70°F into a 40% solution. The steam pressure inside the steam chest is 40 psig. Determine the pounds of steam needed per hour if the exit strong caustic preheats the entering weak caustic in a heat exchanger, leaving the heat exchanger at 100°F.

**13.12 A 50% by weight sulfuric acid solution is to be made by mixing the following:
a. Ice at 32°F
b. 80% H_2SO_4 at 100°F
c. 20% H_2SO_4 at 100°F
How much of each must be added to make 1000 lb of the 50% solution with a final temperature of 100°F if the mixing is adiabatic?

*13.13 Saturated steam at 300°F is blown continuously into a tank of 30% H_2SO_4 at 70°F. What is the highest concentration of liquid H_2SO_4 that can result from this process?

**13.14 One thousand pounds of 10% NaOH solution at 100°F are to be fortified to 30% NaOH by adding 73% NaOH at 200°F. How much 73% solution must be used? How much cooling must be provided so that the final temperature will be 70°F?

13.15* A mixture of ammonia and water in the vapor phase, saturated at 250 psia and containing 80% by weight ammonia, is passed through a condenser at a rate of 10,000 lb/hr. Heat is removed from the mixture at the rate of 5,800,000 Btu/hr while the mixture passes through a cooler. The mixture is then expanded to a pressure of 100 psia and passes into a separator. A flowsheet of the process is given in Figure P13.15. If the heat loss from the equipment to the surroundings is neglected, determine the composition of the liquid leaving the separator by material and energy balances.

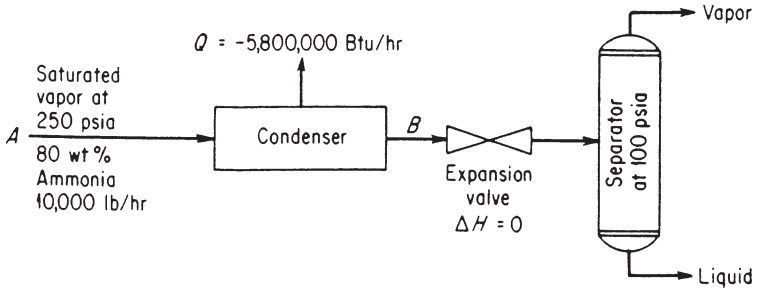


Figure P13.15