$$+ 0.5 \int_{298}^{T} (25.59 + 13.25 \times 10^{-3}T - 4.20 \times 10^{-6}T^2)\, dT$$

$$+ 3.76 \int_{298}^{T} (27.02 + 5.81 \times 10^{-3}T - 0.29 \times 10^{-6}T^2)\, dT$$

$$295{,}571 = 141.14T + 35.37 \times 10^{-3}T^2 - 5.81 \times 10^{-6}T^3 - 45{,}047$$

the solution to which is (by Newton's method starting at $T = 2000$ K)

$$T = 1828 \text{ K}$$

Self-Assessment Test

1. Calculate the theoretical flame temperature when hydrogen burns with 400% excess dry air at 1 atm. The reactants enter at 100°C.

Thought Problems

1. Would burning a fuel with oxygen or with air yield a higher adiabatic flame temperature?
2. A recent news article said:

> Two workers were killed and 45 others hurt when a blast at the ____________ refinery shook a neighborhood and shot flames 500 feet into the air. Hydrogen from a "cracker unit" that separates crude oil into such products as gasoline and diesel fuel burned at temperatures from 4,000 to 5,000 degrees in the 9:50 A.M. accident at the refinery. The fire was put out about an hour later.

Is the temperature cited reasonable?

4.8 HEATS OF SOLUTION AND MIXING

4.8-1 Enthalpy Changes for Mixtures

Your objectives in studying this section are to be able to:

1. Distinguish between ideal solutions and real solutions.
2. Calculate the heat of mixing, or the heat of dissolution, at standard conditions given the moles of the materials forming the mixture.
3. Calculate the standard integral heat of solution.
4. Define the standard integral heat of solution at infinite dilution.
5. Apply the energy balance to problems in which the heat of mixing is significant.

So far in our energy calculations, we have been considering each substance to be a completely pure and separate material. The physical properties of an ideal solution or mixture may be computed from the sum of the properties in question for the individual components. For gases, mole fractions can be used as weighting values, or, alternatively, each component can be considered to be independent of the others. In most instances so far in this book we have used the latter procedure. Using the former technique, as we did in a few instances, we could write down, for the heat capacity of an ideal mixture,

$$C_{p\,\text{mixture}} = x_A C_{p_A} + x_B C_{p_B} + x_C C_{p_C} + \cdots \tag{4.52}$$

or, for the enthalpy,

$$\Delta \hat{H}_{\text{mixture}} = x_A \Delta \hat{H}_A + x_B \Delta \hat{H}_B + x_C \Delta \hat{H}_C + \cdots \tag{4.53}$$

These equations are applicable to ideal mixtures only.

When two or more pure substances are mixed to form a gas or liquid solution, we frequently find heat is absorbed or evolved from the system upon mixing. Such a solution would be called a "real" solution. Per mole of solute

$$\Delta \hat{H}^\circ_{\text{final solution}} - \Delta \hat{H}^\circ_{\text{initial components}} = \Delta \hat{H}^\circ_{\text{mixing}} \tag{4.54}$$

The **heat of mixing** ($\Delta \hat{H}^\circ_{\text{mixing}}$) (i.e, the enthaply change on mixing) has to be determined experimentally, but can be retrieved from tabulated experimental (smoothed) results, once such data are available. This type of energy change has been given the formal name ***heat of solution*** when one substance dissolves in another; and there is also the negative of the heat of solution, the ***heat of dissolution,*** for a substance that separates from a solution.

Tabulated data for heats of solution appear in Table 4.12 in terms of energy *per mole of solute* for consecutively added quantities of solvent to the solute; the gram mole refers to the gram mole of solute. Heats of solution are somewhat similar to heats of reaction in that an energy change takes place because of differences in the forces of attraction of the solvent and solute molecules. Of course, these energy changes are much smaller than those we find accompanying the breaking and combining of chemical bonds. Heats of solution are conveniently treated in exactly the same way as are the heats of reaction in the energy balance.

The solution process can be represented by an equation such as the following:

$$HCl(g) + 5H_2O \longrightarrow HCl \cdot 5H_2O$$

or

$$HCl(g) + 5H_2O \longrightarrow HCl(5H_2O)$$

$$\Delta H^\circ_{\text{soln}} = -64{,}047 \text{ J/g mol HCl(g)}$$

The expression $HCl(5H_2O)$ means that 1 mole of HCl has been dissolved in 5 moles of water, and the enthalpy change for the process is −64,047 J/g mol of HCl. Table 4.12 shows the heat of solution for various cumulative numbers of moles of water added to 1 mole of HCl.

The ***standard integral heat of solution*** is the cumulative $\Delta H^\circ_{\text{soln}}$ as shown in the next to last column for the indicated number of molecules of water. As succes-

TABLE 4.12 Heat of Solution of HCl* (at 25°C and 1 atm)

Composition	Total moles H_2O added to 1 mole HCl	$-\Delta\hat{H}^{\circ}$ for each incremental step (J/g mol HCl) $= -\Delta\hat{H}^{\circ}_{\text{dilution}}$	Integral heat of solution: cumulative $-\Delta\hat{H}^{\circ}$ (J/g mol HCl)	Heat of formation $-\Delta\hat{H}_f^{\circ}$ (J/g mol HCl)
HCl(g)	0			92,311
$HCl \cdot 1H_2O(aq)$	1	26,225	26,225	118,536
$HCl \cdot 2H_2O(aq)$	2	22,593	48,818	141,129
$HCl \cdot 3H_2O(aq)$	3	8,033	56,851	149,161
$HCl \cdot 4H_2O(aq)$	4	4,351	61,202	153,513
$HCl \cdot 5H_2O(aq)$	5	2,845	64,047	156,358
$HCl \cdot 8H_2O(aq)$	8	4,184	68,231	160,542
$HCl \cdot 10H_2O(aq)$	10	1,255	69,486	161,797
$HCl \cdot 15H_2O(aq)$	15	1,503	70,989	163,300
$HCl \cdot 25H_2O(aq)$	25	1,276	72,265	164,576
$HCl \cdot 50H_2O(aq)$	50	1,013	73,278	165,589
$HCl \cdot 100H_2O(aq)$	100	569	73,847	166,158
$HCl \cdot 200H_2O(aq)$	200	356	74,203	166,514
$HCl \cdot 500H_2O(aq)$	500	318	74,521	166,832
$HCl \cdot 1000H_2O(aq)$	1,000	163	74,684	166,995
$HCl \cdot 50{,}000H_2O(aq)$	50,000	146	75,077	167,388
$HCl \cdot \infty H_2O$		67	75,144	167,455

*To convert to cal/g mol multiply by 0.2390.

SOURCE: *National Bureau of Standards Circular 500,* U.S. Government Printing Office, Washington, D.C., 1952.

sive increments of water are added to the mole of HCl, the cumulative heat of solution (the integral heat of solution) increases, but the incremental enthalpy change decreases as shown in Table 4.12. Note that both the reactants and products have to be at standard conditions. The heat of dissolution would be just the negative of these values. The integral heat of the solution is plotted in Fig. 4.20, and you can see that an asymptotic value is approached as the solution becomes more and more dilute. At infinite dilution this value is called the ***standard integral heat of solution at infinite dilution*** and is −75,144 J/g mol of HCl. What can you conclude about the reference state for the heat of solution of pure HCl from Fig. 4.20? In Appendix H are other tables presenting standard integral heat of solution data and the heats of formation of

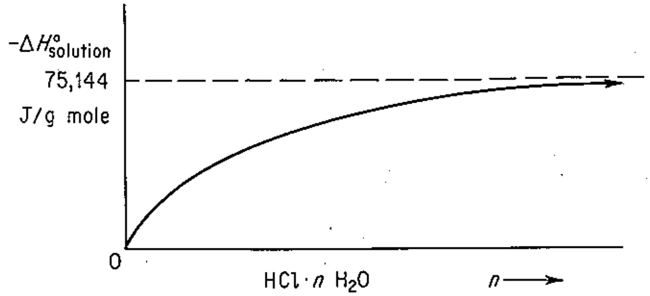


Figure 4.20 Integral heat of solution of HCl in water.

solutions. Since the energy changes for heats of solution are point functions, you can easily look up any two concentrations of HCl and find the energy change caused by adding or subtracting water. For example, if you mix 1 mole of $HCl \cdot 15\,H_2O$ and 1 mole of $HCl \cdot 5H_2O$, you obtain 2 moles of $HCl \cdot 10H_2O$, and the total enthalpy change at 25°C 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.

To calculate the standard heat of formation of a solute in solution, you proceed as follows. What is the standard heat of formation of 1 g mol of HCl in 5 g mol of H_2O? We treat the solution process in an identical fashion to a chemical reaction:

$$\begin{array}{lllr} & & & \textit{J/g mol} \\ \hline \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) & = HCl(g) & A: & \Delta\hat{H}^\circ_f = -92{,}311 \\ \underline{HCl(g) + 5H_2O} & \underline{= HCl(5H_2O)} & \underline{B:} & \underline{\Delta\hat{H}^\circ_{\text{soln}} = -64{,}047} \\ \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) + 5H_2O & = HCl(5H_2O) & A + B: & \Delta\hat{H}^\circ_f = -156{,}358 \end{array}$$

It is important to remember that the heat of formation of H_2O itself does not enter into the calculation. The heat of formation of HCl in an infinitely dilute solution is

$$\Delta\hat{H}^\circ_f = -92{,}311 - 75{,}144 = -167{,}455 \text{ kJ/g mol}$$

Another type of heat of solution which is occasionally encountered is the partial molal heat of solution. Information about this thermodynamic property can be found in most standard thermodynamic texts or in books on thermochemistry, but we do not have the space to discuss it here.

One point of special importance concerns the formation of water in a chemical reaction. When water participates in a chemical reaction in solution as a reactant or product of the reaction, you must include the heat of formation of the water as well as the heat of solution in the energy balance. Thus, if 1 mole of HCl reacts with 1 mole of sodium hydroxide to form water and the reaction is carried out in only 2 moles of water to start with, it is apparent that you will have 3 moles of water at the end of the process. Not only do you have to take into account the heat of reaction when the water is formed, but there is also a heat of solution contribution. If gaseous HCl reacts with crystalline sodium hydroxide and the product is 1 mole of gaseous water vapor, you could employ the energy balance without worrying about the heat of solution effect.

EXAMPLE 4.42 Application of Heat of Solution Data

Hydrochloric acid is an important industrial chemical. To make aqueous solutions of it of commercial grade (known as *muriatic acid*), purified HCl(g) is absorbed in water in a tantalum absorber in a continuous process. How much heat must be removed from the absorber per 100 kg of product if hot HCl(g) at 120°C is fed into water in the absorber as shown in

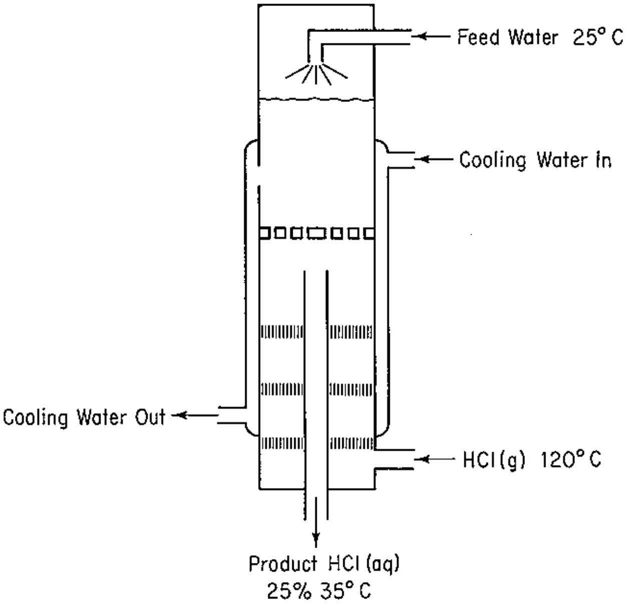


Figure E4.42

Fig. E4.42? 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.

Solution

Steps 1, 2, and 3 We need to add to the figure enthalpy data which are easiest to get per mole of HCl. Consequently, we will first convert the product into moles of HCl and moles of H_2O.

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

Basis: 100 kg of product

Ref. temperature: 25°C

Steps 5 and 6 Equation (4.40) can be used to calculate $Q = \Delta H$, and both the initial and final enthalpies of all the streams are known or can be calculated directly, hence the problem has a unique solution. The kg and moles of HCl in and out, and the water in and out, have been calculated above.

Step 3 (Continued) The enthalpy values for the streams are [C_p for the HCl(g) is from Table E.1; C_p for the product is approximately 2.7 J/(g)(°C)]:

Stream	ΔH
Feed H_2O	0
HCl(g)	$685 \int_{25}^{120} C_p\, dT = 685(2747) = 1.883 \times 10^6$ J
HCl(aq)	$10^5 \int_{25}^{35} C_p\, dT = 2.7 \times 10^6$ J

By interpolation, the heat of solution data from Table 4.12 give

$$\Delta \hat{H}^\circ_{\text{solution}} = -65{,}442 \text{ J/g mol HCl}$$

$$\Delta H^\circ_{\text{solution}} = (-65{,}442)(685) = -4.4828 \times 10^7 \text{ J}$$

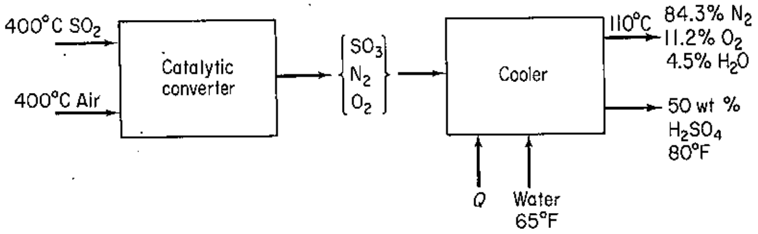
Steps 7, 8, and 9

$$\begin{aligned} Q = \Delta H &= \Delta H_{\text{final products}} - \Delta H_{\text{entering feeds}} + \Delta H^\circ_{\text{solution}} \\ &= 2.7 \times 10^6 - 1.883 \times 10^6 + (-4.4828 \times 10^7) \\ &= -4.4 \times 10^7 \text{ J} \end{aligned}$$

The negative value of Q means heat is removed from the system.

Self-Assessment Test

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. **(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 H_2O in the reference state?
4. Use the heat of solution data in Appendix H 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 *mole-%* 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 $10H_2O$ to $1H_2SO_4$.
5. Calculate the heat that must be added or removed per ton of 50 wt % H_2SO_4 produced by the process shown.



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?