4.3 CALCULATION OF ENTHALPY CHANGES (WITHOUT CHANGE OF PHASE)

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

1. Calculate enthalpy (and internal energy) changes (excluding phase changes) from heat capacity equations, graphs and charts, tables, and computer data bases given the initial and final states of the material.
2. Become familiar with the steam tables and their use both in SI and American engineering units.
3. Ascertain the reference state for enthalpy values from the data source

Now that we have examined sources of heat capacity values, we turn to the details of the calculation of enthalpy and internal energy changes. We omit for the moment consideration of phase changes and examine solely the problem of how to calculate enthalpy (or internal energy) changes that take place in a single phase, that is, how to calculate the so-called **"sensible heat"** changes. Sensible heat is the enthaply difference (normally for a gas) between some reference temperature and the temperature of the material under consideration, excluding any enthalpy differences for phase changes that are termed latent heats and discussed in Sec. 4.4. We examine four procedures:

1. Use of heat capacity equations
2. Use of tables
3. Use of enthalpy charts
4. Use of computer data bases

4.3-1 How to Employ Heat Capacity Equations

Recall that if we use Eq.(4.8), $\Delta\hat{H}$ is the area under the curve in Fig. 4.8:

$$\int_{\hat{H}_1}^{\hat{H}_2} d\hat{H} = \Delta\hat{H} = \int_{T_1}^{T_2} C_p \, dT$$

If the heat capacity is expressed in the form $C_p = a + bT + cT^2$, then

$$\Delta\hat{H} = \int_{T_1}^{T_2} (a + bT + cT^2)\, dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) \tag{4.10}$$

If a different functional form of the heat capacity is available, the integration result

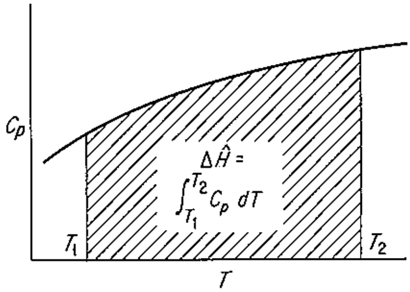

Figure 4.8 Calculation of enthalpy change.

will be different. Equation (4.10) can be stored in a data base and used to calculate enthalpy changes for a single phase as easily as the heat capacity equation can be stored. Can you develop an expression similar to Eq. (4.10) for $\Delta\hat{U}$ based on a polynomial expression for C_v as a function of temperature? Will the right-hand side look exactly the same as Eq. (4.10)?

EXAMPLE 4.9 Calculation of $\Delta\hat{H}$ for a Gas Mixture Using Heat Capacity Equations

The conversion of solid wastes to innocuous gases can be accomplished in incinerators in an environmentally acceptable fashion. However, the hot exhaust gases must be cooled or diluted with air. An economic feasibility study indicates that solid municipal waste can be burned to a gas of the following composition (on a dry basis):

CO_2	9.2%
CO	1.5%
O_2	7.3%
N_2	82.0%
	100.0%

What is the enthalpy difference for this gas per lb mol between the bottom and the top of the stack if the temperature at the bottom of the stack is 550°F and the temperature at the top is 200°F? Ignore the water vapor in the gas. Because these are ideal gases, you can neglect any energy effects resulting from the mixing of the gaseous components.

Solution

Heat capacity equations from Table E.2 [T in °F; C_p = Btu/(lb mol)(°F)] are

N_2: $C_p = 6.895 + 0.7624 \times 10^{-3}T - 0.7009 \times 10^{-7}T^2$

O_2: $C_p = 7.104 + 0.7851 \times 10^{-3}T - 0.5528 \times 10^{-7}T^2$

CO_2: $C_p = 8.448 + 5.757 \times 10^{-3}T - 21.59 \times 10^{-7}T^2 + 3.059 \times 10^{-10}T^3$

CO: $C_p = 6.865 + 0.8024 \times 10^{-3}T - 0.7367 \times 10^{-7}T^2$

Basis: 1.00 lb mol of gas

By multiplying these equations by the respective mole fraction of each component, and then adding them together, you can save time in the integration.

N_2: $0.82(6.895 + 0.7624 \times 10^{-3}T - 0.7009 \times 10^{-7}T^2)$

O_2: $0.073(7.104 + 0.7851 \times 10^{-3}T - 0.5528 \times 10^{-7}T^2)$

CO_2: $0.092(8.448 + 5.757 \times 10^{-3}T - 21.59 \times 10^{-7}T^2 + 3.059 \times 10^{-10}T^3)$

CO: $0.015(6.865 + 0.8024 \times 10^{-3}T - 0.7367 \times 10^{-7}T^2)$

$$C_{p_{\text{net}}} = 7.053 + 1.2242 \times 10^{-3}T - 2.6124 \times 10^{-7}T^2 + 0.2814 \times 10^{-10}T^3$$

$$\begin{aligned}\Delta\hat{H} &= \int_{550}^{200} C_p\,dT = \int_{550}^{200} (7.053 + 1.2242 \times 10^{-3}T - 2.6124 \times 10^{-7}T^2 + 0.2814 \times 10^{-10}T^3)\,dT \\ &= 7.053[(200) - (550)] + \frac{1.2242 \times 10^{-3}}{2}[(200)^2 - (550)^2] \\ &\quad - \frac{2.6124 \times 10^{-7}}{3}[(200)^3 - (550)^3] \\ &\quad + \frac{0.2814 \times 10^{-10}}{4}[(200)^4 - (550)^4] \\ &= -2468.6 - 160.7 + 13.8 - 0.633 \\ &= -2616 \text{ Btu/lb mol gas}\end{aligned}$$

4.3-2 Tabular Data

When the values of the physical properties used in your calculations must be accurate, you might well turn to tables. Tables can cover ranges of physical properties well beyond the range applicable for a single equation. Because the most commonly measured properties are temperature and pressure, tables for pure compounds usually are organized in columns and rows, with T and p being the independent variables. If the intervals between table entries are close enough, linear interpolation between entries is reasonably accurate.

Steam tables of all varieties are cited in several of the references in Table 4.5. Tables of the enthalpies for some important compounds at 1 atmosphere will be found in Appendix D.

If you remember that enthalpy values are all relative to some reference state, you can make enthalpy difference calculations merely by subtracting the initial enthalpy from the final enthalpy for any two sets of conditions as shown in the following examples.

EXAMPLE 4.10 Calculation of Enthalpy Change Using Tabulated Enthalpy Values

Calculate the enthalpy change for 1 kg mol of N_2 gas which is heated at a constant pressure of 100 kPa from 18°C to 1100°C.

Solution

We will use the data in Table 4.4 (the pressure is about 1 atm).

$$\text{at } 1100°\text{C} \Leftrightarrow 1373\text{K}: \quad \Delta\hat{H} = 34{,}715 \text{ kJ/kg mol (by interpolation)}$$

$$\text{at } 18°\text{C} \Leftrightarrow 291 \text{ K}: \quad \Delta\hat{H} = 524 \text{ kJ/kg mol}$$

Basis: 1 kg mol of N_2

$$\Delta\hat{H} = 34{,}715 - 524 = 34{,}191 \text{ kJ/kg mol}$$

Tables 4.3 and 4.4 list typical enthalpy data for the combustion gases. Some sources of enthalpy data are listed in Table 4.5. The most common source of enthalpy data for water is the steam tables which are reproduced in Appendix C1 and on a sheet that can be found inside the back cover.

To make use of the steam tables, you must first locate the region of the phase diagram in which the state lies. The tables are organized so that the saturation properties are given separately from the properties of superheated steam and subcooled liquid. Examine the large set of tables in the back of the book. In addition, the saturation properties are presented in two ways: (1) the saturation pressure is given at even intervals for easy interpolation, and (2) the saturation temperature given at even intervals for the same reason.

You can find the region in which a particular state lies by referring to one of the two tables for saturation properties. If, at the given T or P, the given specific intensive property lies outside the range of properties that can exist for saturated liquid, saturated vapor, or their mixtures, the state must be in either the superheated or the subcooled region. For example, look at a brief extract from the steam tables in SI units:

		Specific volume (m^3/kg)			Enthalpy (kJ/kg)		
P_{sat}(kPa)	T_{sat}(°C)	v_l	v_{lg}	v_g	h_l	h_{lg}	h_g
101.325	100.0	0.001043	1.672	1.673	419.5	2256.0	2675.6
200.0	120.2	0.001061	0.8846	0.8857	504.7	2201.5	2706.2

For each saturation pressure, the corresponding saturation temperature (boiling point) is given along with the values of specific volume and enthalpy for both saturated liquid and saturated vapor. The volume and enthalpy value in the middle column designated by the subscript lg is the difference between the saturated vapor and saturated liquid states, and will be discussed in the next section.