Chapter Three - Calculation of Enthalpy Changes

Phase Transitions
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Phase Transitions

phase transitions occur from the solid to the

liquid phase, and from the liquid to the gas phase, and the reverse? During these transitions very large changes in the value of the enthalpy (and internal energy) for a substance occur, changes called **latent heat** changes, because they occur without any noticeable change in temperature. Because of the relatively large enthalpy change associated with phase transitions, it is important to accurately ascertain latent heats when applying energy balances that involve them. For a single phase, the enthalpy varies as a function of the temperature, as illustrated in Figure 1. The enthalpy changes that take place within a single phase are often called **"sensible heat"** changes.

The enthalpy changes for the phase transitions are termed **heat of fusion** (for melting), ΔH_{fusion}, and **heat of vaporization** (for vaporization), ΔH_v. The word "heat" has been carried alone by custom from very old experiments in which enthalpy changes were calculated from experimental data that frequently involved heat transfer. Enthalpy of fusion and vaporization would be the proper terms, but they are not widely used. **Heat of condensation** is the negative of the heat of vaporization and the **heat of solidification** is the negative of the heat of fusion. The **heat of sublimation** is the enthalpy change from solid directly to vapor.

The overall enthalpy change of a pure substance, as illustrated in Figure 1, can be formulated as follows (per unit mass starting below the fusion temperature):

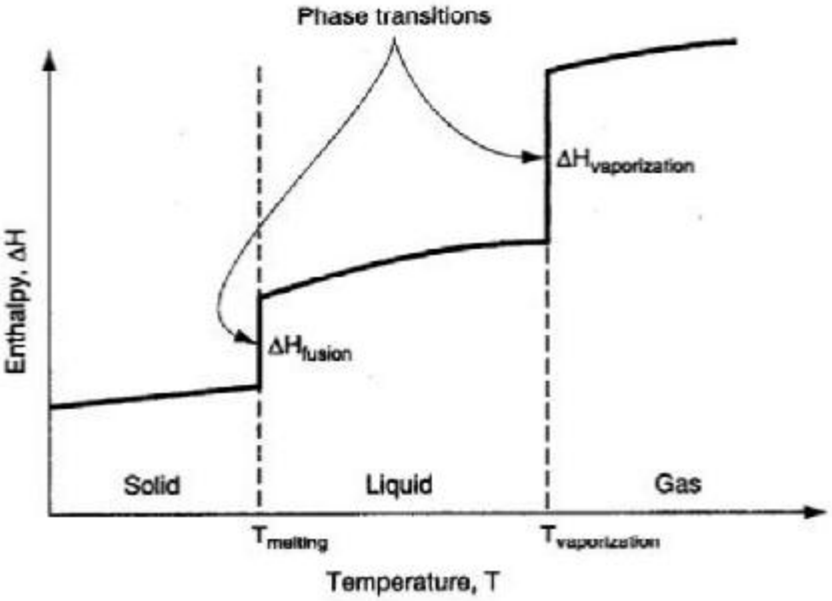


Figure 1 Enthalpy changes of a pure substance as a function of temperature. The vertical lines represent the "latent changes" that occur during a phase transition.

$$\Delta\hat{H}=\hat{H}(T)-\hat{H}(T_{\text{ref}})=\underbrace{\int_{T_{\text{ref}}}^{T_{\text{fusion}}} C_{p,\text{solid}}\,dT}_{\text{Sensible heat of solid}}+\underbrace{\Delta\hat{H}_{\text{fusion at }T_{\text{fusion}}}}_{\text{Melting}}+\underbrace{\int_{T_{\text{fusion}}}^{T_{\text{vaporization}}} C_{p,\text{liquid}}\,dT}_{\text{Sensible heat of liquid}}$$

$$+\underbrace{\Delta\hat{H}_{\text{vaporization at }T_{\text{vap}}}}_{\text{Vaporization}}+\underbrace{\int_{T_{\text{vap}}}^{T} C_{p,\text{vapor}}\,dT}_{\text{Sensible heat of vapor}} \qquad (1)$$

In tables such as the steam tables, all of the respective enthalpy changes shown in Equation (1), including the phase transitions, are built into the tabulated data. Changes in ΔU can be calculated by an equation analogous to Equation (1) with C_v substituted for C_p, and values of the internal energy phases transitions substituted for the values of the enthalpies of the phase transitions.

Equations to Estimate Heats of Vaporization

1. The Clapeyron Equation The **Clapeyron equation** is an exact thermodynamic relationship between the slope of the vapor-pressure curve and the molar heat of vaporization and the other variables listed below:

$$\frac{dp^*}{dT} = \frac{\Delta \hat{H}_v}{T(\hat{V}_g - \hat{V}_l)} \quad \text{or} \quad \frac{dp^*}{d(\ln T)} = \frac{\Delta \hat{H}_v}{\hat{V}_g - \hat{V}_l} \qquad (2)$$

where p^* = vapor pressure

T = absolute temperature

$\Delta \hat{H}_v$ = molar heat of vaporization at T

$\hat{V}_i$ = molar volume of gas or liquid as indicated by the subscript g or l

Figure 2 shows how the value of the slope $dp / d(\ln T)$ can be used to estimate the specific heat of vaporization. Any consistent set of units may be used.

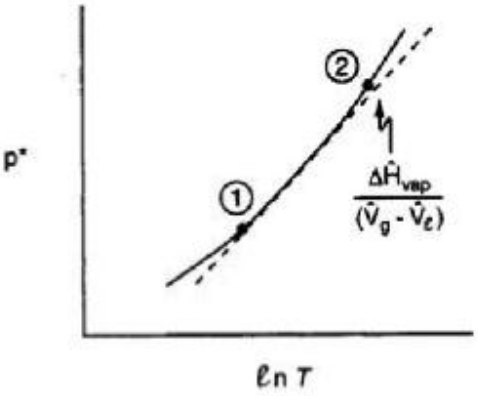


Figure 2 $\Delta \hat{H}_v$ is directly related to the slope of the plot of p^* versus ℓnT, and varies with T.

Equation (2) can be used to calculate $\Delta \hat{H}_v$, and to check the internal consistency of data if a function for the vapor pressure of a substance is known so that you can evaluate dp^*/dT. If you assume that

(a) $\hat{V}_l$ is negligible in comparison with $\hat{V}_g$.

(b) The ideal gas law is applicable for the vapor: $\hat{V}_g = RT/p^*$

Then

$$d\,\ell n p^* = \frac{dp^*}{p^*} = \frac{\Delta \hat{H}_v dT}{RT^2} \qquad (3)$$

If you further assume that $\Delta \hat{H}_v$ is constant over the temperature range of interest, integration of Equation (3) yields the **Clausius-Clapeyron equation**

$$\log_{10}\frac{p_1^*}{p_2^*} = \frac{\Delta\hat{H}_v}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (4)$$

Alternately, you can differentiate Antoine's equation to get $d\,\ell n(p^*)/d\left(\frac{1}{T}\right)$ and combine Antoine's equation with Equation (2). to get ΔH_v.

2. Chen's Equation An equation that yields values of $\Delta\hat{H}_v$ (in kJ/g mol) to within 2% is Chen's equation*:

$$\Delta H_v = RT_b\left(\frac{3.978\,(T_b/T_c) - 3.938 + 1.555\ln p_c}{1.07 - (T_b/T_c)}\right) \qquad (.5)$$

where T_b is the normal boiling point of the liquid in K, T_c is the critical temperature in K, and p_c is the critical pressure in atmospheres.

3. Riedel's Equation**

$$\Delta H_v = 1.093RT_c\left[\frac{T_b}{T_c}\frac{(\ln p_c - 1)}{(0.930 - (T_b/T_c))}\right] \qquad (6).$$

4. Watson's Equation Watson† found empirically that below the critical temperature the ratio of two heats of vaporization could be related by

$$\frac{\Delta\hat{H}_{v_2}}{\Delta\hat{H}_{v_1}} = \left(\frac{1 - T_{r_2}}{1 - T_{r_1}}\right)^{0.38} \qquad (7)$$

where $\Delta\hat{H}_{v_1}$ = heat of vaporization of a pure liquid at T_1

$\Delta\hat{H}_{v_2}$ = heat of vaporization of the same liquid at T_2

Therefore, it is recommended that when you need a heat of vaporization for an energy balance calculation, you use the heat of vaporization at the normal boiling point from the physical property and use Equation (7) to adjust for temperature difference from the normal boiling point.

For example, let's use the heat of vaporization of water at 100°C for which $\Delta\hat{H}_v = 2256.1$ kJ/kg to calculate the heat of vaporization of water at 600 K. For water, $T_c = 647.4$ K:

$$\frac{\Delta\hat{H}_{v,600}}{\Delta\hat{H}_{v,373}} = \left[\frac{(1 - \frac{600}{647.4})}{(1 - \frac{373}{647.4})}\right]^{0.38} = 0.551$$

$$\Delta\hat{H}_{v,600} = 1244 \text{ kJ/kg}$$

EXAMPLE 23.2 Comparison of Various Sources to Estimate the Heat of Vaporization

Use (a) the Clausius-Clapeyron equation, (b) Chen's equation, and (c) Riedel's equation to estimate the heat of vaporization of acetone at its normal boiling point, and compare with the experimental value of 30.2 kJ/g mol listed in Appendix C.

Solution

The basis is 1 g mol. You have to look up some data for acetone in Appendix D:

Normal boiling point:	329.2 K
T_c:	508.0 K
p_c:	47.0 atm

The next step is to calculate some of the values of the variables in the estimation equations

$$T_b/T_c = \frac{329.2}{508.0} = 0.648$$

$$\ell n\, p_c = \ell n(47.0) = 3.85$$

Using the Clayperon equation plus Antoine's equation:

From Equation (.2)

$$d\,\ell n\,(p^*) = \frac{\Delta \hat{H}_v dT}{RT^2} \qquad \text{(a)}$$

and differentiating the Antoine equation

$$d\,\ell n\,(p^*) = \frac{B}{(C+T)^2}dT \qquad \text{(b)}$$

Combination of Equations (a) and (b) gives

$$\Delta H_v = \frac{RBT^2}{(C+T)^2} \qquad \text{(c)}$$

From Appendix G

$$B = 2940.46 \qquad C = -35.93$$

$$\Delta H_v = \frac{8.314\times 10^{-3}}{}\Bigg|\frac{2940.46}{}\Bigg|\frac{(329.2)^2}{(-35.93+392.2)^2}$$

$$= 29.63 \text{ kJ/g mol} \qquad \text{(low by 1.9\%)}$$

Using Chen's equation:

From Equation (5).

$$\Delta H_v = \frac{8.314 \times 10^{-3}\ \text{kJ}}{(\text{g mol})(\text{K})}\bigg|\frac{329.2\ \text{K}}{}\bigg|\frac{[(3.978)(0.648) - 3.938 + (1.555)(3.85)]}{1.07 - 0.648}$$

$= 30.0$ kJ/g mol (insignificant error)

Using Riedel's equation:

From Equation (6)

$$\Delta H_v = 1.093(8.314 \times 10^{-3})(508.0)\left[(0.648)\frac{(3.85 - 1)}{(0.930 - 0.648)}\right]$$

$= 30.23$ kJ/g mol (negligible error)

Heat Capacity Equations

we explained that the enthalpy change for a substance in a single phase (**not for the phase transitions**) can be calculated using the **heat capacity**

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p\, dT \qquad (8)$$

If C_p is constant, $\Delta \hat{H} = C_p\, \Delta T$ where $\Delta T = T_2 - T_1$.

Figure .3 illustrates how $\Delta \hat{H}$ is the area between two limits under the C_p function.

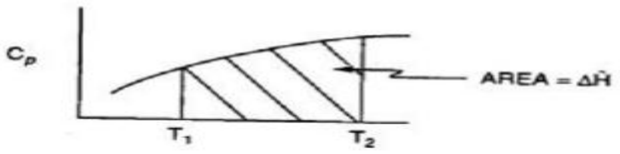


Figure 3 $\Delta \hat{H}$ interpreted as the area obtained by integrating $C_p(T)$ between two temperature limits.

For ideal gases a simple relation exists between C_p and C_v because U and H are functions of temperature only:

$$p\hat{V} = RT$$

$$\hat{H} = \hat{U} + p\hat{V} = \hat{U} + RT$$

Differentiate $\hat{H}$ with respect to temperature

$$C_p = \left(\frac{d\hat{H}}{dT}\right) = \left(\frac{d\hat{U}}{dT}\right) + R = C_v + R \qquad (9)$$

For ideal gas mixtures, the heat capacity (per mole) of the mixture is the mole-weighted average of the heat capacities of the components (x_i is the mole fraction of component i):

$$C_{p_{avg}} = \sum_{i=1}^{n} x_i C_{p_i} \qquad (10)$$

Most of the equations for the heat capacities of solids, liquids, and gases are empirical. You usually find that the heat capacity at constant pressure, C_p, is expressed as a function of temperature for a specified range of temperature. A power series in temperature, with constants a, b, c, and so on, is typically used to model the temperature dependence of C_p. For example

$$C_p = a + bT + cT^2 \qquad (11)$$

where the temperature may be expressed in degrees Celsius, degrees Fahrenheit, degrees Rankine, or degrees kelvin. Since the heat capacity equations are valid only over moderate temperature ranges, it is possible to have equations of different types represent the experimental heat capacity data with almost equal accuracy. **Be wary of extrapolation beyond the designated range of validity for C_p.**

Given the heat capacity equation, for example, Equation (11), you can calculate the enthalpy change per unit mole or mass by integrating the heat capacity equation with respect to temperature

$$\Delta\hat{H} = \int_{T_1}^{T_2} (a + bT + cT^2)dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) \qquad (12)$$

EXAMPLE 23.3 Conversion of Units in a Heat Capacity Equation

The heat capacity equation for CO_2 gas in the temperature range 0 to 1500 K is

$$C_p = 2.675 \times 10^4 + 42.27\,T - 1.425 \times 10^{-2}\,T^2$$

with C_p expressed in J/(kg mol)(ΔK) and T in K. Convert this equation into a form so that the heat capacity will be expressed over the entire temperature range in Btu/(lb mol)(°F) with T in °F.

Solution

Changing a heat capacity equation from one set of units to another is merely a problem in the *conversion of units. Each term in the heat capacity equation must have the same units as the lefthand side of the equation. To avoid confusion in the conversion, you must remember to distinguish between the temperature symbol that in one usage represents temperature, and the usage of the same symbol to represent temperature difference. In the conversions below we shall distinguish between the temperature and the temperature difference for clarity.*

First, multiply each side of the given equation for C_p by appropriate conversion factors to convert J/(kg mol)(ΔK) to (Btu/lb mol)(Δ°F). Multiply the lefthand side by the factor in the square brackets.

$$\frac{C_p\,\text{J}}{(\text{kg mol})(\Delta K)} \times \left[\frac{1\ \text{Btu}}{1055\ \text{J}}\left|\frac{1\ \Delta\text{K}}{1.8\ \Delta°\text{R}}\right|\frac{1\ \Delta°\text{R}}{1\ \Delta°\text{F}}\left|\frac{0.4536\ \text{kg}}{1\ \text{lb}}\right.\right] \rightarrow C_p \frac{\text{Btu}}{(\text{lb mol})(\Delta°\text{F})}$$

and multiply the righthand side by the same set of conversion factors.

Next, substitute the relation between the temperature in K and the temperature in °F

$$T_K = \frac{T_{°R}}{1.8} = \frac{T_{°F} + 460}{1.8}$$

into the given equation for C_p where T appears.

Finally, carry out the indicated mathematical operations, and consolidate quantities to get

$$C_p = 8.702 \times 10^{-3} + 4.66 \times 10^{-6} T_{°F} - 1.053 \times 10^{-9} T_{°F}^2$$

EXAMPLE 23.5 Calculation of $\Delta \hat{H}$ for a Gas Mixture Using Heat Capacity Equations for Each Component

The conversion of solid wastes to innocuous gases can be accomplished in incinerators in an environmentally acceptable fashion. However, the hot exhaust gases often 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. You can neglect any energy effects resulting from the mixing of the gaseous components.

Solution

Basis: 1 lb mol of gas

The heat capacity equations are [T in °F; C_p = Btu/(lb mol)(°F)]

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, but they can be integrated separately.

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

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

$$\Delta H = \int_{550}^{200}(7.053 + 1.2242 \times 10^{-3}T - 2.6124 \times 10^{-7}T^2 + 0.2814 \times 10^{-10}T^3)dT$$

$$= 7.053[(200) - (550)] + \frac{1.2242 \times 10^{-3}}{2}[(200)^2 - (550)^2]$$

$$-\frac{2.6124 \times 10^{-7}}{3}[(200)^3 - (550)^3] + \frac{0.2814 \times 10^{-10}}{4}[(200)^4 - (500)^4]$$

$$= -2468.6 - 160.7 + 13.8 - 0.633 = -2616 \text{ Btu/lb mol gas}$$

Now that you have become acquainted with both enthalpy changes for phase transitions and sensible heat, it is time to combine these concepts so that you can calculate enthalpy changes including phase changes. Look at Figure 5, which shows the transition of water from −30°C to 130°C.

We want to determine the value at 130°C of $\Delta\hat{H}$ on the vertical axis, starting with −30°C as the reference point of zero. As shown in Equation (1), you add the values of the enthalpies of the phase transition to the ΔH values for the sensible heats obtained by integrating the heat capacity equations for ice, liquid water, and water vapor, respectively.

$$\Delta\hat{H}_{T_{\text{ref}}}^{T_{\text{final}}} = \hat{H}(T_{\text{final}}) - \hat{H}(T_{\text{ref}}) = \int_{T_{\text{ref}}}^{T_{\text{fusion}}} C_{p,\text{ ice}}dT + \Delta\hat{H}_{\text{fusion, 0°C}}$$
$$+ \int_{T_{\text{fusion}}}^{T_{\text{vaporization}}} C_{p,\text{ liquid water}}dT + \Delta\hat{H}_{\text{vaporization, 100°C}} \qquad (13)$$
$$+ \int_{T_{\text{vaporization}}}^{T_{\text{final}}} C_{p,\text{ water vapor}}dT$$

For the case in Figure 5, $T_{\text{fusion}} = 0°\text{C}$ and $T_{\text{vaporization}} = 100°\text{C}$. Values of $\Delta\hat{H}_{\text{fusion}}$ and $\Delta\hat{H}_{\text{vaporization}}$ are shown in the figure.

Let's calculate the enthalpy change for 1 kg of water from −30°C to 130°C, using the data in Figure 5 plus values for C_p of

ice	23.7 J/g mol
liquid water	75.4 J/g mol
water vapor	33.9 J/g mol

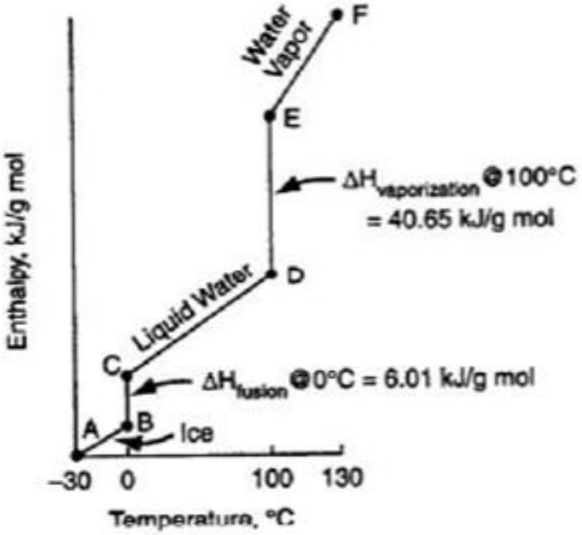


Figure.5 The change of enthalpy of water from −30°C to 130°C.

$$\Delta\hat{H}_{-30^\circ C}^{130^\circ C} = \hat{H}(130^\circ C) - \hat{H}(-30^\circ C) = (23.7)(0-(-30) + 6.01 + (75.4)(100-0)$$
$$+40.65 + (33.9)(130 - 100) = 55{,}930 \text{ J/g mol}$$

Tables and Charts to Retrieve Enthalpy Values

Tables listing smoothed experimental data can accurately 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 of enthalpies (and internal energies) 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. For example, look at the following extract from the SI Steam Tables. If you want to calculate the enthalpy of saturated steam at 307 K by linear interpolation, as explained , you would carry out the following computation:

$$H_{307} = H_{305} + \frac{H_{310} - H_{305}}{T_{310} - T_{305}}(T_{307} - T_{305}) = 2559.1 + \frac{2568.2 - 2559.1}{310 - 305} = (307 - 305) = 2557.5$$

PROPERTIES OF SATURATED WATER

T	Press.	Volume, m³/kg		Enthalpy, kJ/kg		
K	kPa	V_l	V_g	H_l	H_{vap}	H_g
273.16	0.6113	0.001000	206.1	0.0	2500.9	2500.9
275	0.6980	0.001000	181.7	7.5	2496.8	2504.3
280	0.9912	0.001000	130.3	28.1	2485.4	2513.5
285	1.388	0.001001	94.67	48.8	2473.9	2522.7
290	1.919	0.001001	69.67	69.7	2462.2	2531.9
295	2.620	0.001002	51.90	90.7	2450.3	2541.0
300	3.536	0.001004	39.10	111.7	2438.4	2550.1
305	4.718	0.001005	29.78	132.8	2426.3	2559.1
310	6.230	0.001007	22.91	153.9	2414.3	2568.2
315	8.143	0.001009	17.80	175.1	2402.0	2577.1
320	10.54	0.001011	13.96	196.2	2389.8	2586.0
325	13.53	0.001013	11.04	217.3	2377.6	2594.9
330	17.21	0.001015	8.809	238.4	2365.3	2603.7
335	21.71	0.001018	7.083	259.4	2353.0	2612.4
340	27.18	0.001021	5.737	280.5	2340.5	2621.0

EXAMPLE 23.6 Calculation of the Enthalpy Change of a Gas Using Tabulated Enthalpy Values

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

Solution

Because 100 kPa is essentially 1 atm, you can use the tables in Appendix D6 to calculate the enthalpy change, or use the CD.

At 1100°C (1373K): $\hat{H} = 34.715$ kJ/kg mol (by interpolation)

At 18°C (291K): $\hat{H} = 524$ kJ/kg mol

Basis: 1 kg of N_2

$$\Delta \hat{H} = 34.715 - 0.524 = 34.191 \text{ kJ/kg mol}$$

TABLE D.6 Enthalpies of Combustion Gases* (J/g mol)†

K	N_2	O_2	Air	H_2
273	0	0	0	0
291	524	527	523	516
298	728	732	726	718
300	786	790	784	763
400	3,695	3,752	3,696	3,655
500	6,644	6,811	6,660	6,589
600	9,627	9,970	9,673	9,518
700	12,652	13,225	12,736	12,459
800	15,756	16,564	15,878	15,413
900	18,961	19,970	19,116	18,384
1,000	22,171	23,434	22,367	21,388
1,100	25,472	26,940	25,698	24,426
1,200	28,819	30,492	29,078	27,509
1,300	32,216	34,078	32,501	30,626
1,400	35,639	37,693	35,953	33,789
1,500	39,145	41,337	39,463	36,994
1,750	47,940	50,555	48,325	45,275

EXAMPLE 23.7 Use of the Steam Tables to Calculate Changes in Enthalpy

Steam is cooled from 640°F and 92 psia to 480°F and 52 psia. What is $\Delta \hat{H}$ in Btu/lb?

Solution

The problem asks for the change in $\hat{H}$ from state A to state B as indicated in Figure E23.7.

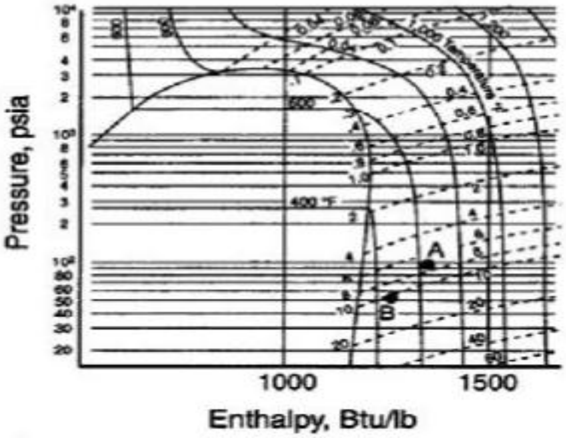
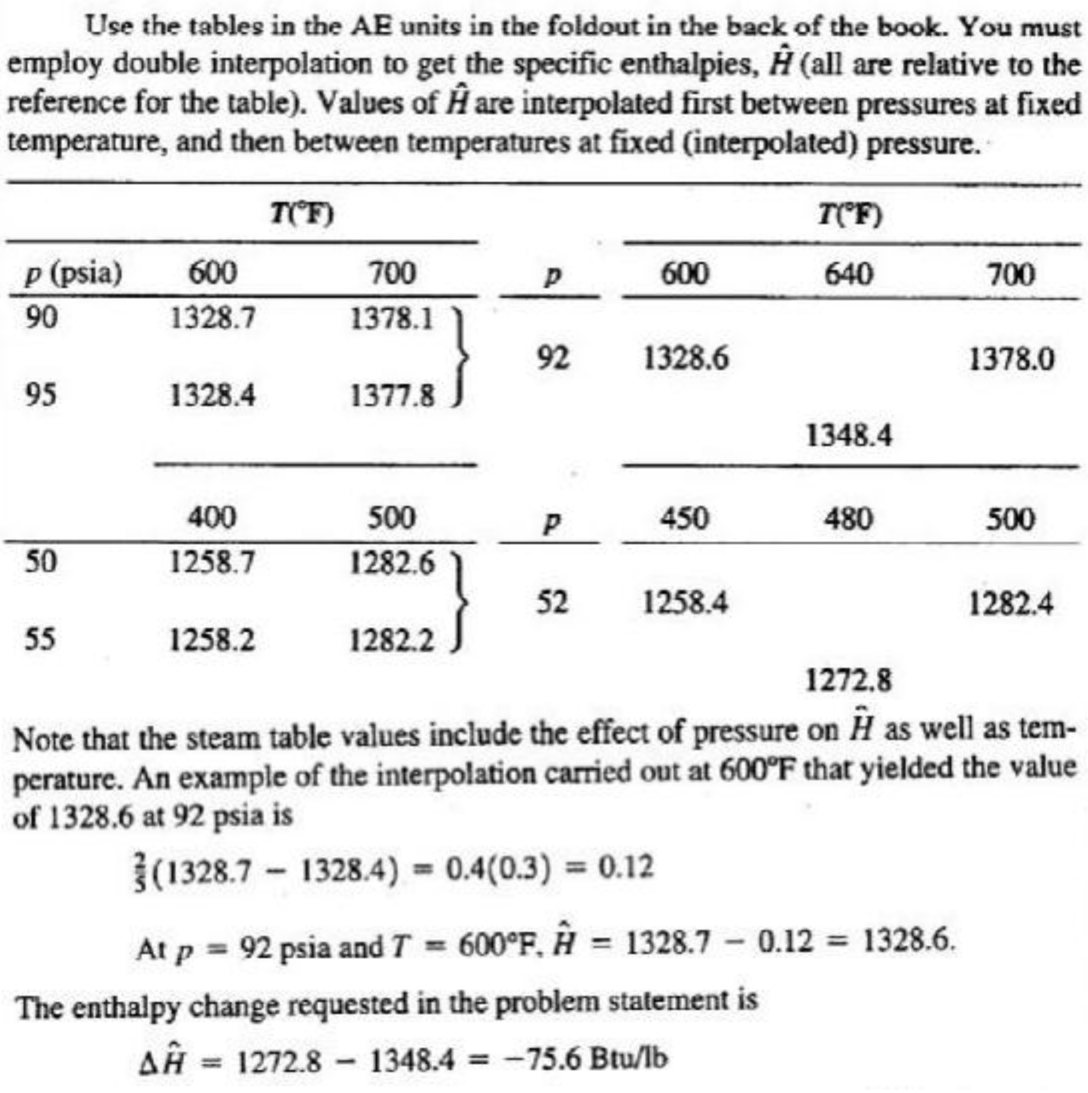


Figure E23.7



Use the tables in the AE units in the foldout in the back of the book. You must employ double interpolation to get the specific enthalpies, $\hat{H}$ (all are relative to the reference for the table). Values of $\hat{H}$ are interpolated first between pressures at fixed temperature, and then between temperatures at fixed (interpolated) pressure.

	T(°F)	
p (psia)	600	700
90	1328.7	1378.1
95	1328.4	1377.8

	T(°F)		
p	600	640	700
92	1328.6		1378.0
		1348.4	

	400	500
50	1258.7	1282.6
55	1258.2	1282.2

p	450	480	500
52	1258.4		1282.4
		1272.8	

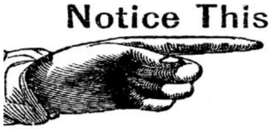
Note that the steam table values include the effect of pressure on $\hat{H}$ as well as temperature. An example of the interpolation carried out at 600°F that yielded the value of 1328.6 at 92 psia is

$$\tfrac{2}{5}(1328.7 - 1328.4) = 0.4(0.3) = 0.12$$

At $p = 92$ psia and $T = 600°\text{F}$, $\hat{H} = 1328.7 - 0.12 = 1328.6$.

The enthalpy change requested in the problem statement is

$$\Delta\hat{H} = 1272.8 - 1348.4 = -75.6 \text{ Btu/lb}$$



Home Work: *Basic Princeples and Calculation in Chemical Engineering*, 7th edition, **Problems of chapter 23, page 708 – 716**.