3.5.3. Enthalpy

The sum of the internal energy U and the pressure multiplied by the volume pV frequently appears in thermo-fluid analyses and so is given the special name, enthalpy, H,

$$\boxed{H := U + pV}. \tag{3.59}$$

Note that enthalpy is a property since U, p, and V are also properties. On a per unit mass basis (making it an intensive property), the enthalpy becomes the specific enthalpy, h,

$$\boxed{h := u + pv}. \tag{3.60}$$

Notes:

(1) It is important to note that the specific internal energies and specific enthalpies in the tables (along with the specific entropies, a property to be discussed later), are calculated with respect to a particular reference state. For example, the internal energy of water is defined to be zero at a saturated liquid state of $0.01\,°C$, i.e., $u_{\text{sat,H2O @ }0.01\,°C} := 0$. Since most thermodynamic analyses involve calculating differences in properties, e.g., Δu, the choice of reference state does not affect the results. For example, if a new reference state is chosen such that $u_{\text{new}} = u_{\text{table}} + c$ where u_{table} is the internal energy found in one of the tables and c is an arbitrary constant, then $\Delta u_{\text{new}} = u_{\text{new,2}} - u_{\text{new,1}} = (u_{\text{table,2}} + c) - (u_{\text{table,1}} + c) = u_{\text{table,2}} - u_{\text{table,1}} = \Delta u_{\text{table}}$. Thus, the choice of reference state is irrelevant.

(2) Property values for compressed liquids are often approximated using the saturated liquid property values at the corresponding temperature, i.e.,

$$v(T, p)_{CL} \approx v_l(T), \tag{3.61}$$
$$u(T, p)_{CL} \approx u_l(T). \tag{3.62}$$

These approximations may be made because in the compressed liquid region, the spacing between isobars is very small as one moves between specific volumes (and specific internal energies), as can be seen in Figure 3.25.

The specific enthalpy may be approximated as,

$$h(T, p)_{CL} \approx u_l(T) + pv_l(T). \tag{3.63}$$

Note that,

$$h_l(T) = u_l(T) + p_{\text{sat}}(T)v_l(T) \implies u_l(T) = h_l(T) - p_{\text{sat}}(T)v_l(T). \tag{3.64}$$

Substituting into Eq. (3.63) gives,

$$h(T, p)_{CL} \approx h_l(T) - p_{\text{sat}}(T)v_l(T) + pv_l(T), \tag{3.65}$$
$$h(T, p)_{CL} \approx h_l(T) + [p - p_{\text{sat}}(T)]v_l(T). \tag{3.66}$$

Notes:

(1) In some cases, $p - p_{\text{sat}}(T)$ is a small value (along with v_l generally being small for saturated liquids) and, thus, $h(T, p)_{CL} \approx h_l(T)$.

(2) Be careful with unit conversions when evaluating Eq. (**??**).

Determine the relative errors in calculating the specific volume, specific internal energy, and specific enthalpy for liquid water at a temperature and pressure of 100 °C and 100 bar, respectively, using thermodynamic property tables and using the saturated liquid state approximations.

SOLUTION:
From the thermodynamic property tables for liquid water at 100 °C and 100 bar (e.g., Table A-5, Moran et al., 7th ed.),

v = $1.0385*10^{-3}$ m^3/kg
u = 416.12 kJ/kg
h = 426.50 kJ/kg

Using the saturated liquid approximations (e.g., Table A-2, Moran et al., 7th ed.),

v ≈ $1.0435*10^{-3}$ m^3/kg at 100 °C
u_l ≈ 418.94 kJ/kg at 100 °C
h ≈ 429.37 kJ/kg at 100 °C, h_l = 419.04 kJ/kg and $p_{sat,100 °C}$ = 1.014 bar

The relative error, ε, in a property, P, is,

$$\varepsilon_P = \frac{P_{approx} - P_{actual}}{P_{actual}} .$$ (1)

Thus, $\varepsilon_v = 0.005$, $\varepsilon_u = 0.007$, and $\varepsilon_h = 0.007$. The error is less than 1% in all cases, implying that the approximations are good ones.

Five kg of water is contained in a piston-cylinder assembly, initially at 5 bar and 240 °C. The water is slowly heated at constant pressure to a final state. If the heat transfer into the water for the process is 2960 kJ, determine the temperature at the final state, in °C, and the work done by the water on the piston, in kJ. Kinetic and potential energy effects are negligible.

SOLUTION:
Apply the 1st Law to the water in the piston,

$$\Delta E_{H2O} = Q_{\underset{H2O}{into}} - W_{\underset{H20}{by}} \ ,$$ (1)

where

$$\Delta E_{H2O} = \Delta U_{H2O} = m(u_2 - u_1).$$ (2)

The specific internal energy at the initial state (state 1) may be found from the thermodynamic tables for water at p_1 = 5 bar and T_1 = 240 °C. Note that saturation temperature for liquid water at 5 bar is 151.86 °C; hence, the water must be in the superheated vapor region since T_1 is greater than the saturation temperature. Using the table,

u_1 = 2707.6 kJ/kg,
v_1 = 0.4646 m^3/kg,
h_1 = 2939.9 kJ/kg.

The work done by the water on the piston is,

$$W_{by \ H2O} = \int_{V_1}^{V_2} p \, dV = p(V_2 - V_1) = pm(v_2 - v_1),$$ (3)

where the pressure is constant ($p_1 = p_2$ = 5 bar) throughout the process. Substituting into Eq.

$$m(u_2 - u_1) = Q_{\underset{H2O}{into}} - pm(v_2 - v_1),$$ (4)

$$m(u_2 + p_2 v_2 - u_1 - p_1 v_1) = Q_{\underset{H2O}{into}} \ ,$$ (5)

$$m(h_2 - h_1) = Q_{\underset{H2O}{into}} \ ,$$ (6)

$$h_2 = h_1 + \frac{Q_{\underset{H2O}{into}}}{m} \ ,$$ (7)

where h is the specific enthalpy of the water. Substituting values,

h_1 = 2939.9 kJ/kg
Q_{into} = 2960 kJ
m = 5 kg
$\Rightarrow h_2$ = 3531.9 kJ/kg

From the thermodynamic two-phase liquid-vapor table for water at p_2 = 5 bar, the saturated vapor specific enthalpy is 2748.7 kJ/kg, which is smaller than h_2. Hence, the water at state 2 will be in the superheated vapor state. Using the thermodynamic superheated vapor table with h_2 and p_2, and interpolating,
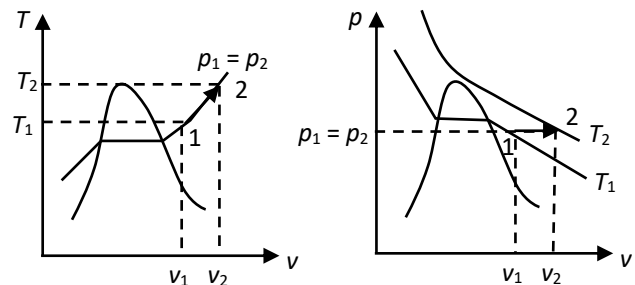
$\boxed{T_2 \ = 522 \ °C}$
v_2 = 0.7314 m^3/kg

Using Eq. (3) and the values for v_1, v_2, m, and p,
$\boxed{W_{by \ H2O} = 667 \ kJ/kg}$

Sketches of the process on T-v and p-v plots are shown.

A closed, rigid tank is initially filled with 0.8 kg of water at 70 bar (abs) and a volume of 0.001 m^3 (state 1). Heat transfer occurs between the water and the surroundings until the pressure in the water is 35 bar (abs) (state 2).
a. Is the initial phase of the water a compressed liquid, saturated, or superheated vapor? Justify your answer.
b. Determine the specific internal energy at the initial state, in kJ/kg.
c. Calculate the specific volume at the final state, in m^3/kg.
d. Is the final phase of the water a compressed liquid, saturated, or superheated vapor? Justify your answer.
e. Determine the final specific internal energy of the water, in kJ/kg.
f. Determine the work done by the water during the process, in kJ.

SOLUTION:
The system is the water as shown in the following figure.
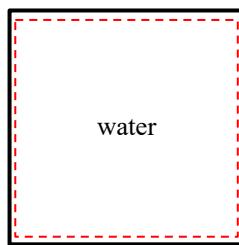
The specific volume at state 1 is,
$$v_1 = \frac{V}{m},$$ (1)
where $V = 0.001$ m^3 and $m = 0.8$ kg. Hence,
$$v_1 = 1.25 \times 10^{-3} \text{ m}^3/\text{kg}.$$ (2)
At a pressure of $p_1 = 70$ bar, the specific volume for a saturated liquid state is 1.3513×10^{-3} m^3/kg (from Table A-3 in Moran et al., 7th ed.). Since the specific volume at state 1 is smaller than this value, state 1 must be in a compressed liquid phase.

Since the water is in a compressed liquid state, we can use the saturated liquid value of the specific internal energy at the same temperature (recall that $u_{CL}(p,T) \approx u_l(T)$) to approximate the actual specific internal energy (found from Table A-3). Since the temperature isn't given we can estimate it from the specific volume. Recall that for a compressed liquid, $v_{CL}(p,T) \approx v_l(T)$. Thus, using Table A-2 in Moran et al., the temperature corresponding to $v_1 = v_{CL} = 1.25 \times 10^{-3}$ m^3/kg is approximately $T = 250$ °C. The corresponding saturated liquid specific internal energy is,
$$u_1 = 1080.4 \text{ kJ/kg}.$$ (3)

The specific volume at state 2 will be identical to the specific volume at state 1 since the tank volume and water mass remain unchanged, i.e.,
$$v_2 = v_1 = 1.25 \times 10^{-3} \text{ m}^3/\text{kg}.$$ (4)

At $p_2 = 35$ bar (abs), the specific volumes for the saturated liquid and saturated vapor states (Table A-3) are, respectively,
$$v_{l2} = 1.2347 \times 10^{-3} \text{ m}^3/\text{kg},$$ (5)
$$v_{v2} = 0.05707 \text{ m}^3/\text{kg}.$$ (6)
The specific volume for state 2 (Eq. (4)) falls between these two values. Hence, state 2 is in a saturated phase.

Since state 2 is in a saturated phase, the specific internal energy is found using the quality at state 2. The quality at state 2 can be found using the specific volume at state 2,

$$v_2 = x_2 v_{v2} + (1 - x_2) v_{l2} \Rightarrow x_2 = \frac{v_2 - v_{l2}}{v_{v2} - v_{l2}}, \tag{7}$$

$x_2 = 2.74 * 10^{-4}.$ (8)

The specific internal energy at the saturated liquid and saturated vapors states (Table A-3) is, respectively,

u_{l2} = 1045.4 kJ/kg, (9)
u_{v2} = 2603.7 kJ/kg. (10)

Hence, the specific internal energy at state 2 is,

$$u_2 = x_2 u_{v2} + (1 - x_2) u_{l2}, \tag{11}$$

$\boxed{u_2 = 1045.8 \text{ kJ/kg}}.$ (12)

Since the volume doesn't change during the process, there is no work done by the water,

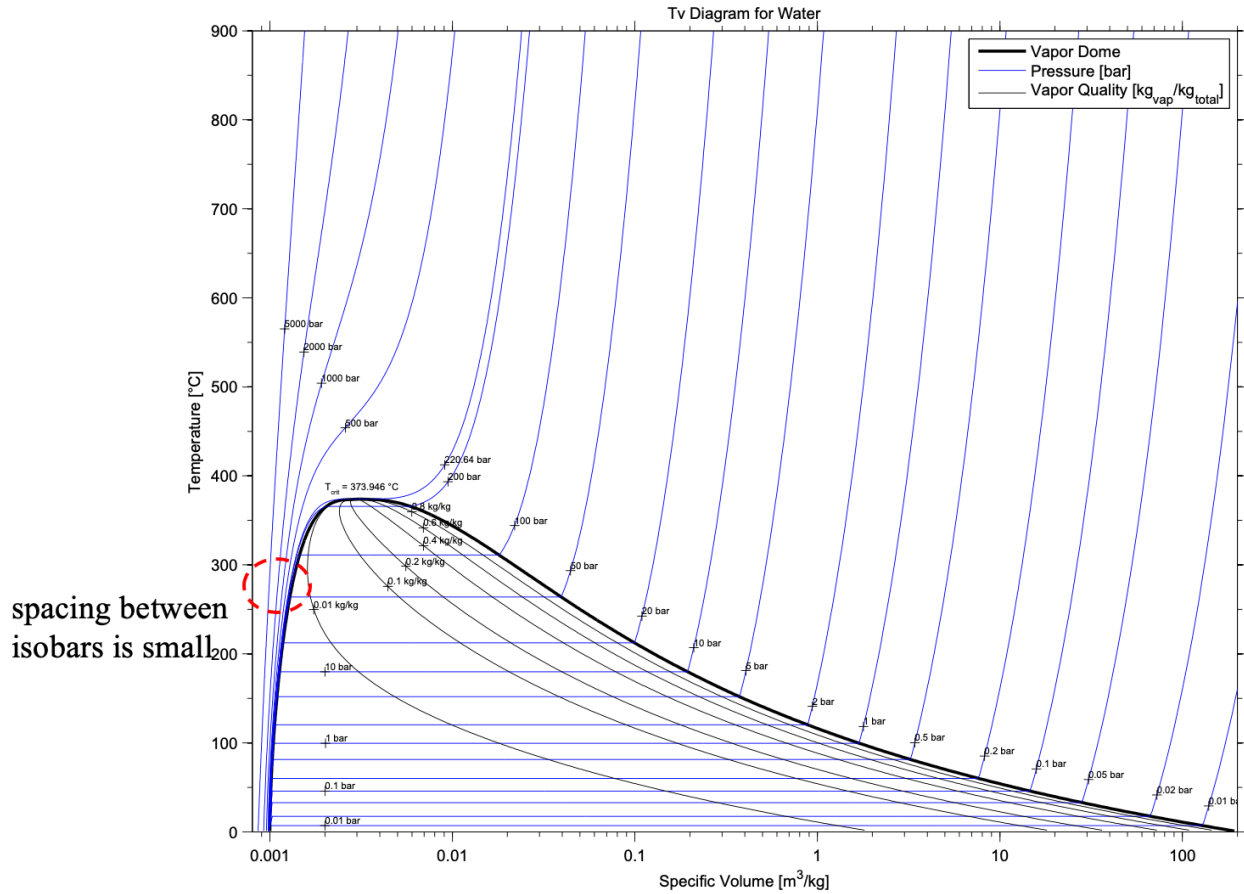$\boxed{W_{\substack{on \\ H_2O}} = 0}.$ (13)

FIGURE 3.25. A T-v plot for water highlighting the close spacing of isobars in the compressed liquid region.

3.5.4. Specific Heat

Recall that internal energy, sensible energy in particular, is related to temperature. Furthermore, we know from experience that some materials heat up at different rates than others. For example, 4.5 kJ of energy added to a 1 kg mass of iron will raise the iron's temperature from 20 °C to 30 °C. To raise 1 kg of water from 20 °C to 30 °C, however, requires 41.8 kJ; about nine times the amount of energy than is required to raise the iron's temperature an equivalent amount.

The property that quantifies the energy storage capability of matter is called the specific heat (aka specific heat capacity). The specific heat of a substance is the energy required to raise the temperature of a unit mass of a substance by one degree. In general, the energy required to raise the temperature of a substance will depend on the process path. Two particular processes of interest are where the system's volume is held constant while energy is added and where the pressure in the system is held constant while energy is added.

The specific heat at constant volume, c_v, is the energy required to raise the temperature of a unit mass by one degree during a constant volume process. For a pure, simple compressible substance with $u(T, v)$, the specific heat at constant volume is defined as,

$$c_v := \left. \frac{\partial u}{\partial T} \right|_v,$$ (3.67)