

## Chapter 2: Properties of Pure Substances

We now turn our attention to the concept of pure substances and the presentation of their data.

### Simple System

A simple system is one in which the effects of motion, viscosity, fluid shear, capillarity, anisotropic stress, and external force fields are absent.

### Homogeneous Substance

A substance that has uniform thermodynamic properties throughout is said to be homogeneous.

### Pure Substance

A pure substance has a homogeneous and invariable chemical composition and may exist in more than one phase.

Examples:

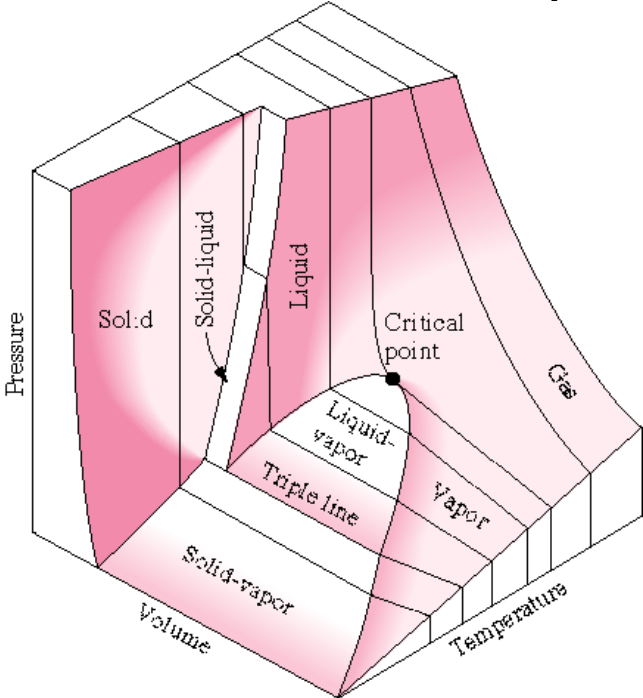
1. Water (solid, liquid, and vapor phases)
2. Mixture of liquid water and water vapor
3. Carbon dioxide,  $\text{CO}_2$
4. Nitrogen,  $\text{N}_2$
5. Mixtures of gases, such as air, as long as there is no change of phase.

### State Postulate

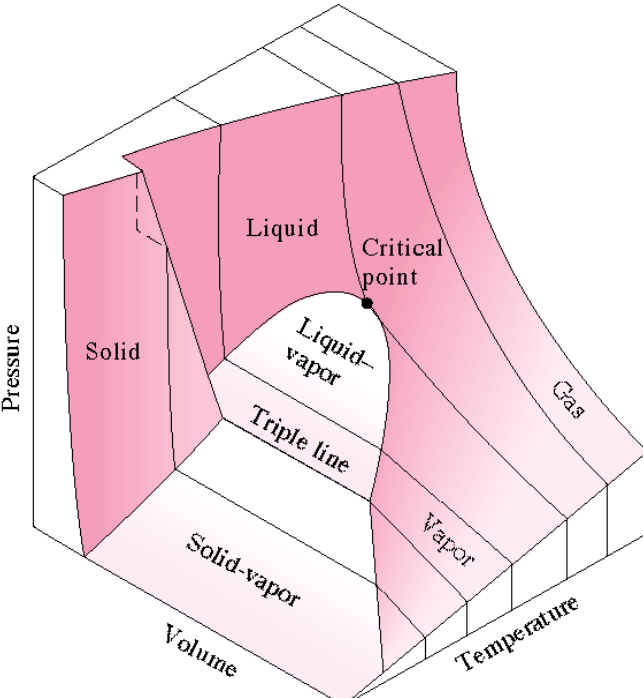
Again, the state postulate for a simple, pure substance states that the equilibrium state can be determined by specifying any two independent intensive properties.

**The  $P$ - $V$ - $T$  Surface for a Real Substance**

◆  **$P$ - $V$ - $T$  Surface for a Substance that contracts upon freezing**



◆  **$P$ - $V$ - $T$  Surface for a Substance that expands upon freezing**



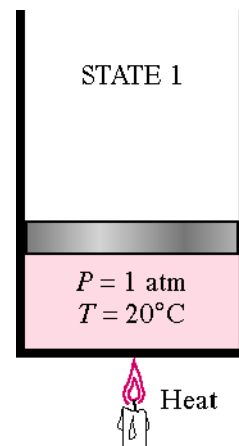
Real substances that readily change phase from solid to liquid to gas such as water, refrigerant-134a, and ammonia cannot be treated as ideal gases in general. The pressure, volume, temperature relation, or equation of state for these substances is generally very complicated, and the thermodynamic properties are given in table form. The properties of these substances may be illustrated by the functional relation  $F(P,v,T)=0$ , called an equation of state. The above two figures illustrate the function for a substance that contracts on freezing and a substance that expands on freezing. Constant pressure curves on a temperature-volume diagram are shown in Figure 2-11. These figures show three regions where a substance like water may exist as a solid, liquid or gas (or vapor). Also these figures show that a substance may exist as a mixture of two phases during phase change, solid-vapor, solid-liquid, and liquid-vapor.

Water may exist in the compressed liquid region, a region where saturated liquid water and saturated water vapor are in equilibrium (called the saturation region), and the superheated vapor region (the solid or ice region is not shown).

Let's consider the results of heating liquid water from 20°C, 1 atm while keeping the pressure constant. We will follow the constant pressure process shown in Figure 2-11. First place liquid water in a piston-cylinder device where a fixed weight is placed on the piston to keep the pressure of the water constant at all times. As liquid water is heated while the pressure is held constant, the following events occur.

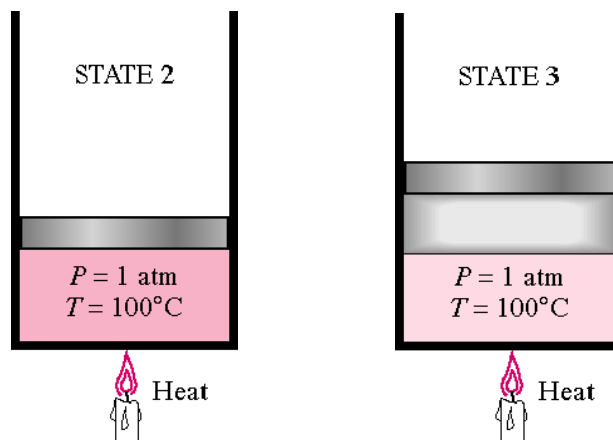
Process 1-2:

The temperature and specific volume will increase from the compressed liquid, or subcooled liquid, state 1, to the saturated liquid state 2. In the compressed liquid region, the properties of the liquid are approximately equal to the properties of the saturated liquid state at the temperature.



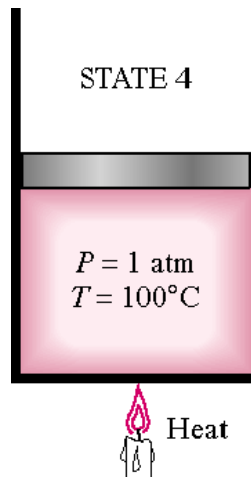
### Process 2-3:

At state 2 the liquid has reached the temperature at which it begins to boil, called the saturation temperature, and is said to exist as a saturated liquid. Properties at the saturated liquid state are noted by the subscript **f** and  $v_2 = v_f$ . During the phase change both the temperature and pressure remain constant (water boils at  $100^\circ\text{C}$  when the pressure is 1 atm or 101.325 kPa). At state 3 the liquid and vapor phase are in equilibrium and any point on the line between states 2 and 3 has the same temperature and pressure.



### Process 3-4:

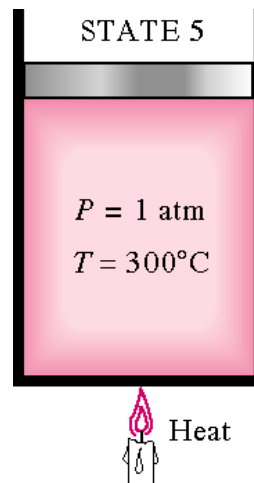
At state 4 a saturated vapor exists and vaporization is complete. The subscript **g** will always denote a saturated vapor state. Note  $v_4 = v_g$ .



Thermodynamic properties at the saturated liquid state and saturated vapor state are given in Table A-4 as the saturated temperature table and Table A-5 as the saturated pressure table. These tables contain the same information. In Table A-4 the saturation temperature is the independent property, and in Table A-5 the saturation pressure is the independent property. The saturation pressure is the pressure at which phase change will occur for a given temperature. In the saturation region the temperature and pressure are dependent properties; if one is known, then the other is automatically known.

Process 4-5:

If the constant pressure heating is continued, the temperature will begin to increase above the saturation temperature, 100 °C in this example, and the volume also increases. State 5 is called a superheated state because  $T_5$  is greater than the saturation temperature for the pressure and the vapor is not about to condense. Thermodynamic properties for water in the superheated region are found in the superheated steam tables, Table A-6.



This constant pressure heating process is illustrated in the following figure.

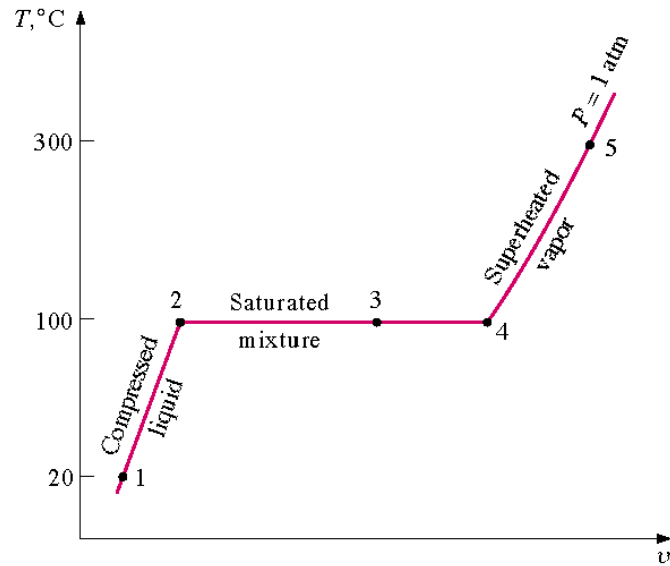
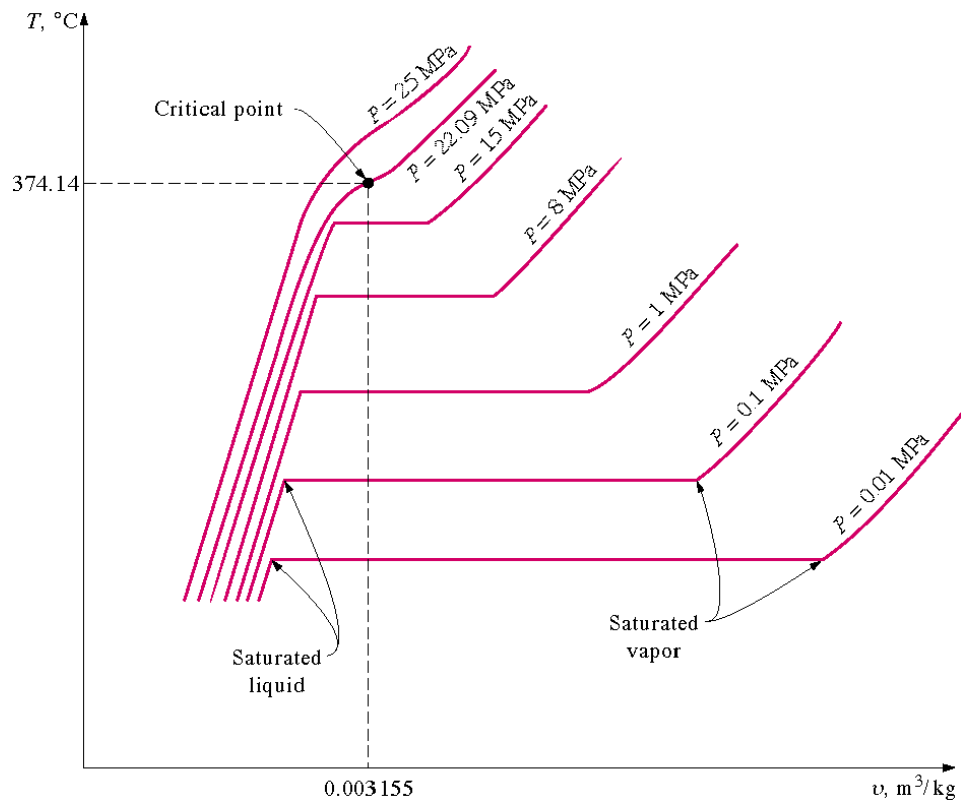
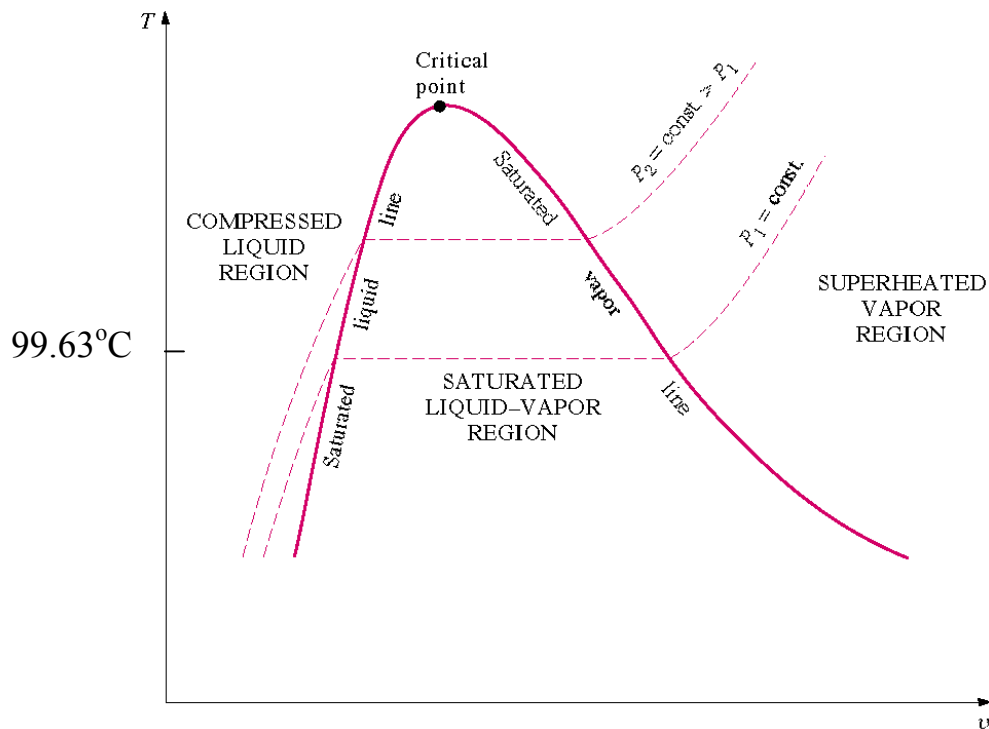


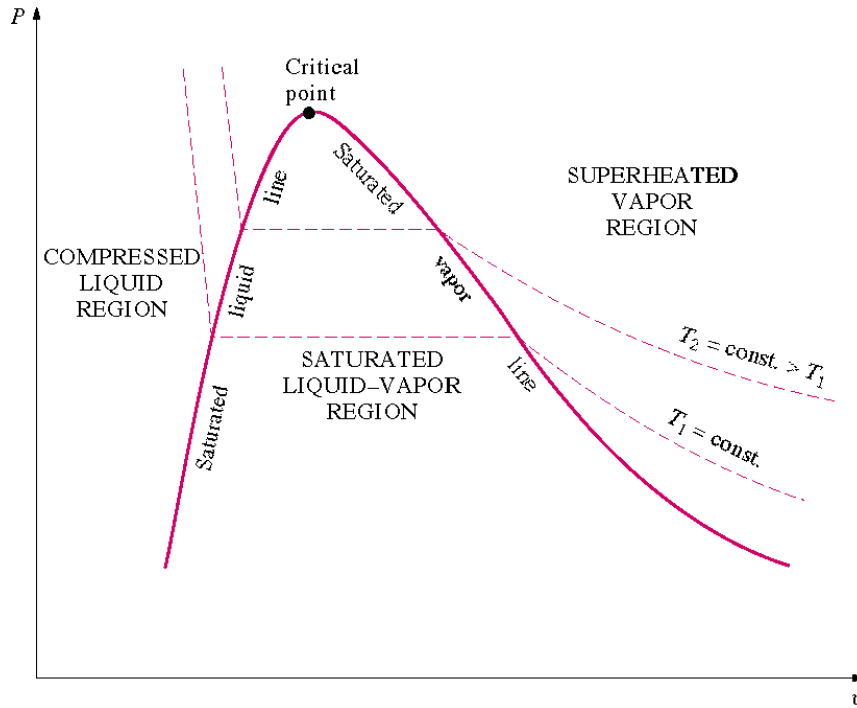
Figure 2-11

Consider repeating this process for other constant pressure lines as shown below.



If all of the saturated liquid states are connected, the saturated liquid line is established. If all of the saturated vapor states are connected, the saturated vapor line is established. These two lines intersect at the critical point and form what is often called the “steam dome.” The region between the saturated liquid line and the saturated vapor line is called by these terms: saturated liquid-vapor mixture region, wet region (i.e., a mixture of saturated liquid and saturated vapor), two-phase region, and just the saturation region. Notice that the trend of the temperature following a constant pressure line is to increase with increasing volume and the trend of the pressure following a constant temperature line is to decrease with increasing volume.





The region to the left of the saturated liquid line and below the critical temperature is called the compressed liquid region. The region to the right of the saturated vapor line and above the critical temperature is called the superheated region. See Table A-1 for the critical point data for selected substances.

Review the  $P$ - $v$  diagrams for substances that contract on freezing and those that expand on freezing given in Figure 2-21 and Figure 2-22.

At temperatures and pressures above the critical point, the phase transition from liquid to vapor is no longer discrete.



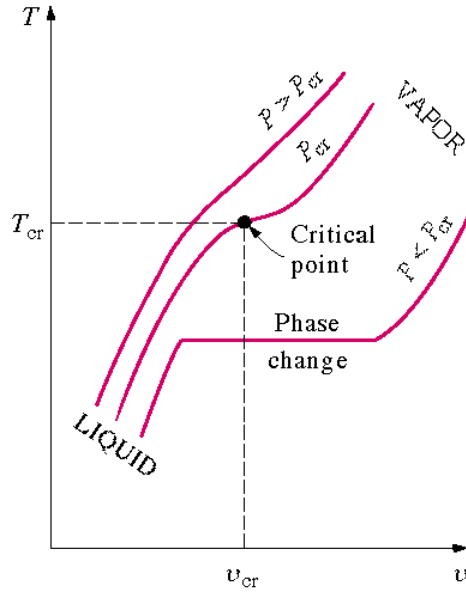
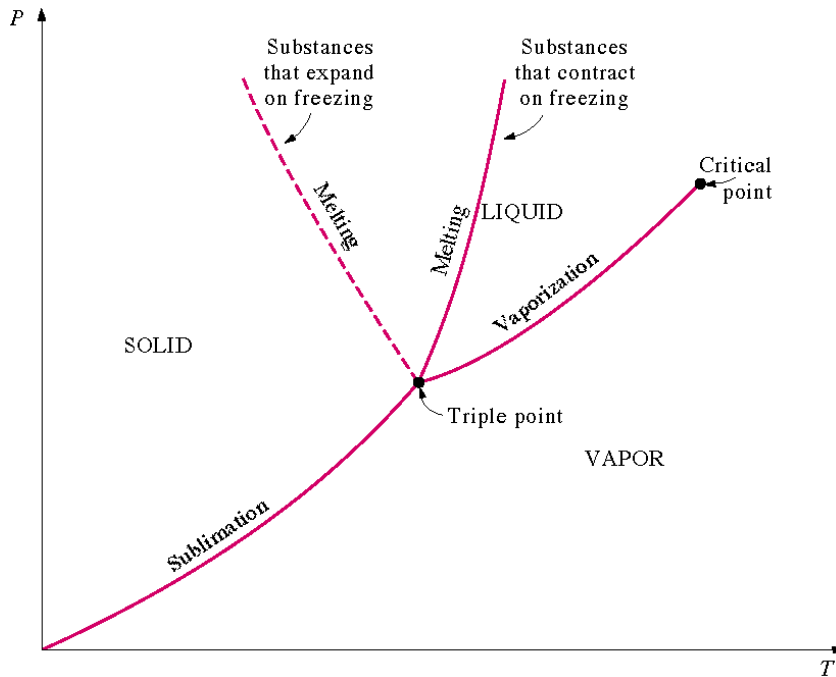


Figure 2-25 shows the  $P$ - $T$  diagram, often called the phase diagram, for pure substances that contract and expand upon freezing.

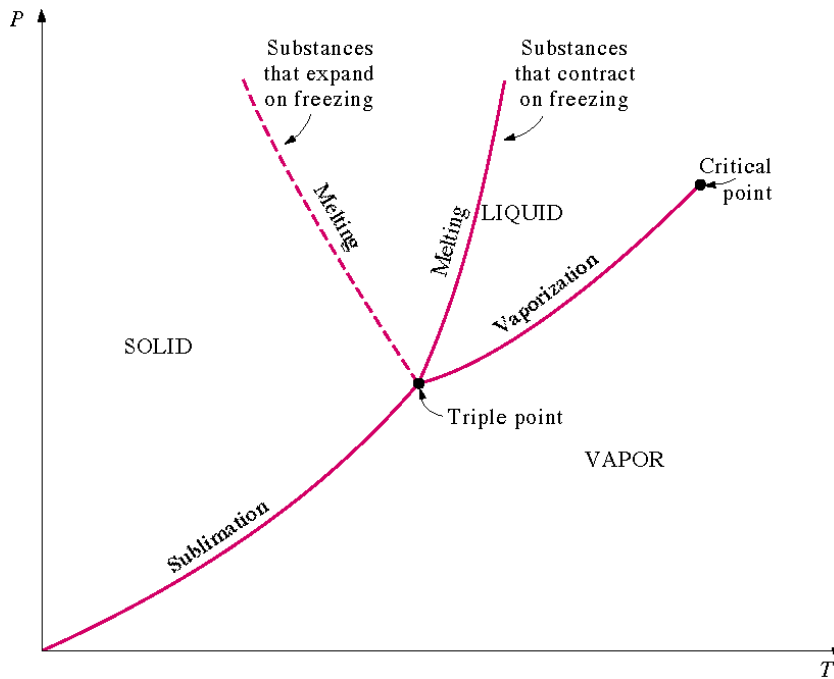


The triple point of water is  $0.01^{\circ}\text{C}$ ,  $0.6113\text{ kPa}$  (See Table 2-3).

The critical point of water is 374.14°C, 22.09 MPa (See Table A-1).

Plot the following processes on the  $P$ - $T$  diagram for water (expands on freezing) and give examples of these processes from your personal experiences.

1. process a-b: liquid to vapor transition
2. process c-d: solid to liquid transition
3. process e-f: solid to vapor transition



## Property Tables

In addition to the temperature, pressure, and volume data, Tables A-4 through A-8 contain the data for the specific internal energy  $u$  the specific enthalpy  $h$  and the specific entropy  $s$ . The enthalpy is a convenient grouping of the internal energy, pressure, and volume and is given by

$$H = U + PV$$

The enthalpy per unit mass is

$$h = u + Pv$$

We will find that the enthalpy  $h$  is quite useful in calculating the energy of mass streams flowing into and out of control volumes. The enthalpy is also useful in the energy balance during a constant pressure process for a substance contained in a closed piston-cylinder device. The enthalpy has units of energy per unit mass, kJ/kg. The entropy  $s$  is a property defined by the second law of thermodynamics and is related to the heat transfer to a system divided by the system temperature; thus, the entropy has units of energy divided by temperature. The concept of entropy is explained in Chapters 5 and 6.

### Saturated Water Tables

Since temperature and pressure are dependent properties using the phase change, two tables are given for the saturation region. Table A-4 has temperature as the independent property; Table A-5 has pressure as the independent property. These two tables contain the same information and often only one table is given.

Sat. Temp. press °C      kPa <i>T</i> <i>P</i> <sub>sat</sub>		Specific volume m <sup>3</sup> /kg	
		Sat. liquid <i>v</i> <sub>f</sub>	Sat. vapor <i>v</i> <sub>g</sub>
85	57.83	0.001 033	2.828
90	70.14	0.001 036	2.361
95	84.55	0.001 040	1.982

**TABLE A-4**

Saturated water—Temperature table

Temp., <i>T</i> , °C	Sat. press., <i>P</i> <sub>sat</sub> , kPa	Specific volume, m <sup>3</sup> /kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/(kg · K)		
		Sat. liquid, <i>v</i> <sub>f</sub>	Sat. vapor, <i>v</i> <sub>g</sub>	Sat. liquid, <i>u</i> <sub>f</sub>	Evap., <i>u</i> <sub>fg</sub>	Sat. vapor, <i>u</i> <sub>g</sub>	Sat. liquid, <i>h</i> <sub>f</sub>	Evap., <i>h</i> <sub>fg</sub>	Sat. vapor, <i>h</i> <sub>g</sub>	Sat. liquid, <i>s</i> <sub>f</sub>	Evap., <i>s</i> <sub>fg</sub>	Sat. vapor, <i>s</i> <sub>g</sub>
0.01	0.6113	0.001000	206.14	0.0	2375.3	2375.3	0.01	2501.3	2501.4	0.000	9.1562	9.1562
5	0.8721	0.001000	147.12	20.97	2361.3	2382.3	20.98	2489.6	2510.6	0.0761	8.9496	9.0257
10	1.2276	0.001000	106.38	42.00	2347.2	2389.2	42.01	2477.7	2519.8	0.1510	8.7498	8.9008
15	1.7051	0.001001	77.93	62.99	2333.1	2396.1	62.99	2465.9	2528.9	0.2245	8.5569	8.7814
20	2.339	0.001002	57.79	83.95	2319.0	2402.9	83.96	2454.1	2538.1	0.2966	8.3706	8.6672
25	3.169	0.001003	43.36	104.88	2304.9	2409.8	104.89	2442.3	2547.2	0.3674	8.1905	8.5580
30	4.246	0.001004	32.89	125.78	2290.8	2416.6	125.79	2430.5	2556.3	0.4369	8.0164	8.4533
35	5.628	0.001006	25.22	146.67	2276.7	2423.4	146.68	2418.6	2565.3	0.5053	7.8478	8.3531
40	7.384	0.001008	19.52	167.56	2262.6	2430.1	167.57	2406.7	2574.3	0.5725	7.6845	8.2570
45	9.593	0.001010	15.26	188.44	2248.4	2436.8	188.45	2394.8	2583.2	0.6387	7.5261	8.1648
50	12.349	0.001012	12.03	209.32	2234.2	2443.5	209.33	2382.7	2592.1	0.7038	7.3725	8.0763
55	15.758	0.001015	9.568	230.21	2219.9	2450.1	230.23	2370.7	2600.9	0.7679	7.2234	7.9913
60	19.940	0.001017	7.671	251.11	2205.5	2456.6	251.13	2358.5	2609.6	0.8312	7.0784	7.9096
65	25.03	0.001020	6.197	272.02	2191.1	2463.1	272.06	2346.2	2618.3	0.8935	6.9375	7.8310
70	31.19	0.001023	5.042	292.95	2176.6	2469.6	292.98	2333.8	2626.8	0.9549	6.8004	7.7553
75	38.58	0.001026	4.131	313.90	2162.0	2475.9	313.93	2321.4	2635.3	1.0155	6.6669	7.6824
80	47.39	0.001029	3.407	334.86	2147.4	2482.2	334.91	2308.8	2643.7	1.0753	6.5369	7.6122
85	57.83	0.001033	2.828	355.84	2132.6	2488.4	355.90	2296.0	2651.9	1.1343	6.4102	7.5445
90	70.14	0.001036	2.361	376.85	2117.7	2494.5	376.92	2283.2	2660.1	1.1925	6.2866	7.4791
95	84.55	0.001040	1.982	397.88	2102.7	2500.6	397.96	2270.2	2668.1	1.2500	6.1659	7.4159
<b>Sat. press., MPa</b>												
100	0.10135	0.001044	1.6729	418.94	2087.6	2506.5	419.04	2257.0	2676.1	1.3069	6.0480	7.3549
105	0.12082	0.001048	1.4194	440.02	2072.3	2512.4	440.15	2243.7	2683.8	1.3630	5.9328	7.2958

For the complete Table A-4, the last entry is the critical point at 374.14 °C.

**TABLE A-5**

**Saturated water—Pressure table**

Press., P kPa	Sat. temp., T <sub>sat</sub> °C	Specific volume, m <sup>3</sup> /kg			Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/(kg · K)		
		Sat. liquid, v <sub>f</sub>	Sat. vapor, v <sub>g</sub>	Sat. liquid, u <sub>f</sub>	Evap., u <sub>fg</sub>	Sat. vapor, u <sub>g</sub>	Sat. liquid, h <sub>f</sub>	Evap., h <sub>fg</sub>	Sat. vapor, h <sub>g</sub>	Sat. liquid, s <sub>f</sub>	Evap., s <sub>fg</sub>	Sat. vapor, s <sub>g</sub>	
0.6113	0.01	0.001000	206.14	0.00	2375.3	2375.3	0.01	2501.3	2501.4	0.0000	9.1562	9.1562	
1.0	6.98	0.001000	129.21	29.30	2355.7	2385.0	29.30	2484.9	2514.2	0.1059	8.8697	8.9756	
1.5	13.03	0.001001	87.98	54.71	2338.6	2393.3	54.71	2470.6	2525.3	0.1957	8.6322	8.8279	
2.0	17.50	0.001001	67.00	73.48	2326.0	2399.5	73.48	2460.0	2533.5	0.2607	8.4629	8.7237	
2.5	21.08	0.001002	54.25	88.48	2315.9	2404.4	88.49	2451.6	2540.0	0.3120	8.3311	8.6432	
3.0	24.08	0.001003	45.67	101.04	2307.5	2408.5	101.05	2444.5	2545.5	0.3545	8.2231	8.5776	
4.0	28.96	0.001004	34.80	121.45	2293.7	2415.2	121.46	2432.9	2554.4	0.4226	8.0520	8.4746	
5.0	32.88	0.001005	28.19	137.81	2282.7	2420.5	137.82	2423.7	2561.5	0.4764	7.9187	8.3951	
7.5	40.29	0.001008	19.24	168.78	2261.7	2430.5	168.79	2406.0	2574.8	0.5764	7.6750	8.2515	
10	45.81	0.001010	14.67	191.82	2246.1	2437.9	191.83	2392.8	2584.7	0.6493	7.5009	8.1502	
15	53.97	0.001014	10.02	225.92	2222.8	2448.7	225.94	2373.1	2599.1	0.7549	7.2536	8.0085	
20	60.06	0.001017	7.649	251.38	2205.4	2456.7	251.40	2358.3	2609.7	0.8320	7.0766	7.9085	
25	64.97	0.001020	6.204	271.90	2191.2	2463.1	271.93	2346.3	2618.2	0.8931	6.9383	7.8314	
30	69.10	0.001022	5.229	289.20	2179.2	2468.4	289.23	2336.1	2625.3	0.9439	6.8247	7.7686	
40	75.87	0.001027	3.993	317.53	2159.5	2477.0	317.58	2319.2	2636.8	1.0259	6.6441	7.6700	
50	81.33	0.001030	3.240	340.44	2143.4	2483.9	340.49	2305.4	2645.9	1.0910	6.5029	7.5939	
75	91.78	0.001037	2.217	384.31	2112.4	2496.7	384.39	2278.6	2663.0	1.2130	6.2434	7.4564	
<b>Press., MPa</b>													
0.100	99.63	0.001043	1.6940	417.36	2088.7	2506.1	417.46	2258.0	2675.5	1.3026	6.0568	7.3594	
0.125	105.99	0.001048	1.3749	444.19	2069.3	2513.5	444.32	2241.0	2685.4	1.3740	5.9104	7.2844	
0.150	111.37	0.001053	1.1593	466.94	2052.7	2519.7	467.11	2226.5	2693.6	1.4336	5.7897	7.2233	
0.175	116.06	0.001057	1.0036	486.80	2038.1	2524.9	486.99	2213.6	2700.6	1.4849	5.6868	7.1717	
0.200	120.23	0.001061	0.8857	504.49	2025.0	2529.5	504.70	2201.9	2706.7	1.5301	5.5970	7.1271	
0.225	124.00	0.001064	0.7933	520.47	2013.1	2533.6	520.72	2191.3	2712.1	1.5706	5.5173	7.0878	
0.250	127.44	0.001067	0.7187	535.10	2002.1	2537.2	535.37	2181.5	2716.9	1.6072	5.4455	7.0527	

For the complete Table A-5, the last entry is the critical point at 22.09 MPa.

**Saturation pressure** is the pressure at which the liquid and vapor phases are in equilibrium at a given temperature.

**Saturation temperature** is the temperature at which the liquid and vapor phases are in equilibrium at a given pressure.

In Figure 2-11, states 2, 3, and 4 are saturation states.

The subscript **fg** used in Tables A-4 and A-5 refers to the difference between the saturated vapor value and the saturated liquid value region. That is,

$$u_{fg} = u_g - u_f$$

$$h_{fg} = h_g - h_f$$

$$s_{fg} = s_g - s_f$$

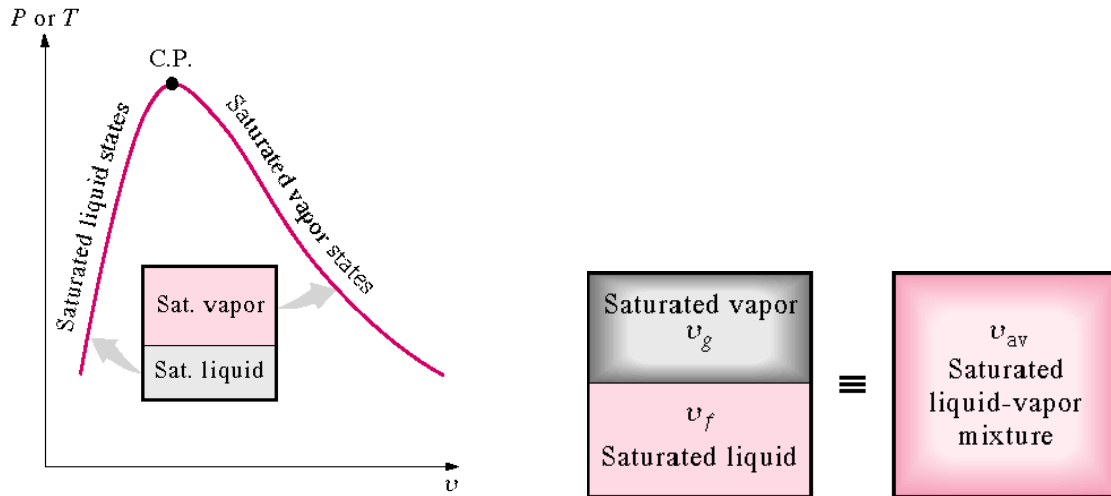
The quantity  $h_{fg}$  is called the enthalpy of vaporization (or latent heat of vaporization). It represents the amount of energy needed to vaporize a unit of mass of saturated liquid at a given temperature or pressure. It decreases as the temperature or pressure increases, and becomes zero at the critical point.

### Quality and Saturated Liquid-Vapor Mixture

Now, let's review the constant pressure heat addition process for water shown in Figure 2-11. Since state 3 is a mixture of saturated liquid and saturated vapor, how do we locate it on the T-v diagram? To establish the location of state 3 a new parameter called the quality  $x$  is defined as

$$x = \frac{\text{mass}_{\text{saturated vapor}}}{\text{mass}_{\text{total}}} = \frac{m_g}{m_f + m_g}$$

The quality is zero for the saturated liquid and one for the saturated vapor ( $0 \leq x \leq 1$ ). The average specific volume at any state 3 is given in terms of the quality as follows. Consider a mixture of saturated liquid and saturated vapor. The liquid has a mass  $m_f$  and occupies a volume  $V_f$ . The vapor has a mass  $m_g$  and occupies a volume  $V_g$ .



We note

$$V = V_f + V_g$$

$$m = m_f + m_g$$

$$V = mv, \quad V_f = m_f v_f, \quad V_g = m_g v_g$$

$$mv = m_f v_f + m_g v_g$$

$$v = \frac{m_f v_f}{m} + \frac{m_g v_g}{m}$$

Recall the definition of quality  $x$

$$x = \frac{m_g}{m} = \frac{m_g}{m_f + m_g}$$

Then

$$\frac{m_f}{m} = \frac{m - m_g}{m} = 1 - x$$



Note, quantity  $1 - x$  is often given the name moisture. The specific volume of the saturated mixture becomes

$$v = (1 - x)v_f + xv_g$$

The form that we use most often is

$$v = v_f + x(v_g - v_f)$$

It is noted that the value of any extensive property per unit mass in the saturation region is calculated from an equation having a form similar to that of the above equation. Let  $Y$  be any extensive property and let  $y$  be the corresponding intensive property,  $Y/m$ , then

$$\begin{aligned} y &= \frac{Y}{m} = y_f + x(y_g - y_f) \\ &= y_f + x y_{fg} \end{aligned}$$

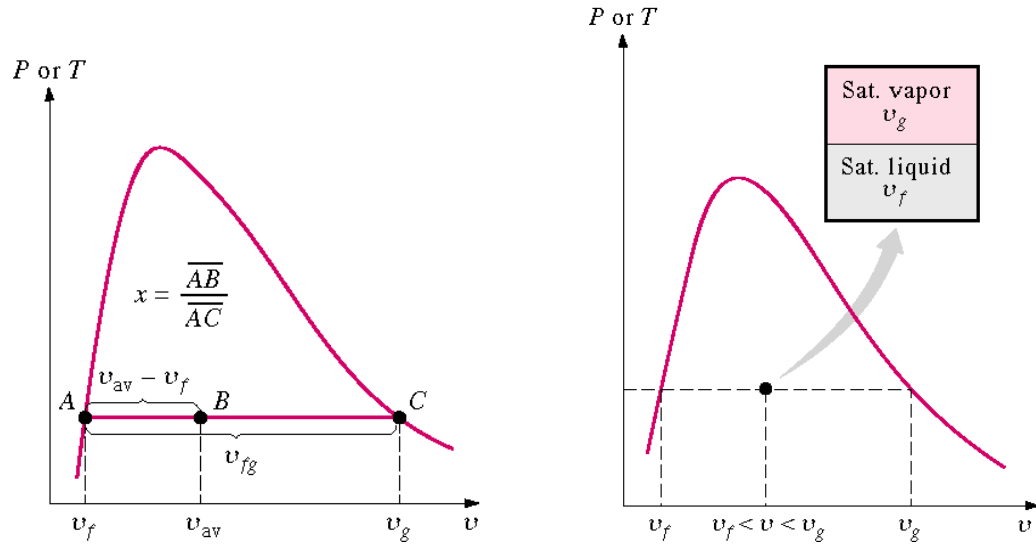
$$\text{where } y_{fg} = y_g - y_f$$

The term  $y_{fg}$  is the difference between the saturated vapor and the saturated liquid values of the property  $y$ ;  $y$  may be replaced by any of the variables  $v$ ,  $u$ ,  $h$ , or  $s$ .

We often use the above equation to determine the quality  $x$  of a saturated liquid-vapor state.

The following application is called the Lever Rule:

$$x = \frac{y - y_f}{y_{fg}}$$



## Superheated Water Table

A substance is said to be **superheated** if the given temperature is greater than the saturation temperature for the given pressure.

State 5 in Figure 2-11 is a superheated state.

In the superheated water Table A-6, T and P are the independent properties. The value of temperature to the right of the pressure is the saturation temperature for the pressure. The first entry in the table is the saturated vapor state at the pressure.

$T, ^\circ\text{C}$	$v,$	$u,$	$h,$
	$\text{m}^3/\text{kg}$	$\text{kJ}/\text{kg}$	$\text{kJ}/\text{kg}$
$P = 0.1 \text{ MPa} (99.63^\circ\text{C})$			
Sat.	1.6940	2506.1	2675.5
100	1.6958	2506.7	2676.2
150	1.9364	2582.8	2776.4
$\vdots$	$\vdots$	$\vdots$	$\vdots$
1300	7.260	4683.5	5409.5
$P = 0.5 \text{ MPa} (151.86^\circ\text{C})$			
Sat.	0.3749	2561.2	2748.7
200	0.4249	2642.9	2855.4
250	0.4744	2723.5	2960.7

**TABLE A-6**

**Superheated water**

$T$ $^\circ\text{C}$	$v$ $\text{m}^3/\text{kg}$	$u$ $\text{kJ}/\text{kg}$	$h$ $\text{kJ}/\text{kg}$	$s$ $\text{kJ}/(\text{kg} \cdot \text{K})$	$v$ $\text{m}^3/\text{kg}$	$u$ $\text{kJ}/\text{kg}$	$h$ $\text{kJ}/\text{kg}$	$s$ $\text{kJ}/(\text{kg} \cdot \text{K})$	$v$ $\text{m}^3/\text{kg}$	$u$ $\text{kJ}/\text{kg}$	$h$ $\text{kJ}/\text{kg}$	$s$ $\text{kJ}/(\text{kg} \cdot \text{K})$
$P = 0.01 \text{ MPa} (45.81^\circ\text{C})^*$				$P = 0.05 \text{ MPa} (81.33^\circ\text{C})$				$P = 0.10 \text{ MPa} (99.63^\circ\text{C})$				
Sat. <sup>1</sup>	14.674	2437.9	2584.7	8.1502	3.240	2483.9	2645.9	7.5939	1.6940	2506.1	2675.5	7.3594
50	14.869	2443.9	2592.6	8.1749								
100	17.196	2515.5	2687.5	8.4479	3.418	2511.6	2682.5	7.6947	1.6958	2506.7	2676.2	7.3614
150	19.512	2587.9	2783.0	8.6882	3.889	2585.6	2780.1	7.9401	1.9364	2582.8	2776.4	7.6134
200	21.825	2661.3	2879.5	8.9038	4.356	2659.9	2877.7	8.1580	2.172	2658.1	2875.3	7.8343
250	24.136	2736.0	2977.3	9.1002	4.820	2735.0	2976.0	8.3556	2.406	2733.7	2974.3	8.0333
300	26.445	2812.1	3076.5	9.2813	5.284	2811.3	3075.5	8.5373	2.639	2810.4	3074.3	8.2158
400	31.063	2968.9	3279.6	9.6077	6.209	2968.5	3278.9	8.8642	3.103	2967.9	3278.2	8.5435
500	35.679	3132.3	3489.1	9.8978	7.134	3132.0	3488.7	9.1546	3.565	3131.6	3488.1	8.8342
600	40.295	3302.5	3705.4	10.1608	8.057	3302.2	3705.1	9.4178	4.028	3301.9	3704.4	9.0976
700	44.911	3479.6	3928.7	10.4028	8.981	3479.4	3928.5	9.6599	4.490	3479.2	3928.2	9.3398
800	49.526	3663.8	4159.0	10.6281	9.904	3663.6	4158.9	9.8852	4.952	3663.5	4158.6	9.5652
900	54.141	3855.0	4396.4	10.8396	10.828	3854.9	4396.3	10.0967	5.414	3854.8	4396.1	9.7767
1000	58.757	4053.0	4640.6	11.0393	11.751	4052.9	4640.5	10.2964	5.875	4052.8	4640.3	9.9764
1100	63.372	4257.5	4891.2	11.2287	12.674	4257.4	4891.1	10.4859	6.337	4257.3	4891.0	10.1659
1200	67.987	4467.9	5147.8	11.4091	13.597	4467.8	5147.7	10.6662	6.799	4467.7	5147.6	10.3463
1300	72.602	4683.7	5409.7	11.5811	14.521	4683.6	5409.6	10.8382	7.260	4683.5	5409.5	10.5183

### Compressed Liquid Water Table

A substance is said to be a **compressed liquid** when the pressure is greater than the saturation pressure for the temperature.

It is now noted that state 1 in Figure 2-11 is called a compressed liquid state because the saturation pressure for the temperature  $T_1$  is less than  $P_1$ .

Data for water compressed liquid states are found in the compressed liquid tables, Table A-7. Table A-7 is arranged like Table A-6, except the saturation states are the saturated liquid states. Note that the data in Table A-7 begins at 5 MPa or 50 times atmospheric pressure.

**TABLE A-7**  
Compressed liquid water

$T$ °C	$v$ m <sup>3</sup> /kg	$u$ kJ/kg	$h$ kJ/kg	$s$ kJ/(kg · K)	$v$ m <sup>3</sup> /kg	$u$ kJ/kg	$h$ kJ/kg	$s$ kJ/(kg · K)
$P = 5 \text{ MPa (263.99°C)}$					$P = 10 \text{ MPa (311.06°C)}$			
Sat.	0.0012859	1147.8	1154.2	2.9202	0.0014524	1393.0	1407.6	3.3596
0	0.0009977	0.04	5.04	0.0001	0.0009952	0.09	10.04	0.0002
20	0.0009995	83.65	88.65	0.2956	0.0009972	83.36	93.33	0.2945
40	0.0010056	166.95	171.97	0.5705	0.0010034	166.35	176.38	0.5686
60	0.0010149	250.23	255.30	0.8285	0.0010127	249.36	259.49	0.8258
80	0.0010268	333.72	338.85	1.0720	0.0010245	332.59	342.83	1.0688
100	0.0010410	417.52	422.72	1.3030	0.0010385	416.12	426.50	1.2992
120	0.0010576	501.80	507.09	1.5233	0.0010549	500.08	510.64	1.5189
140	0.0010768	586.76	592.15	1.7343	0.0010737	584.68	595.42	1.7292
160	0.0010988	672.62	678.12	1.9375	0.0010953	670.13	681.08	1.9317
180	0.0011240	759.63	765.25	2.1341	0.0011199	756.65	767.84	2.1275
200	0.0011530	848.1	853.9	2.3255	0.0011480	844.5	856.0	2.3178
220	0.0011866	938.4	944.4	2.5128	0.0011805	934.1	945.9	2.5039
240	0.0012264	1031.4	1037.5	2.6979	0.0012187	1026.0	1038.1	2.6872
260	0.0012749	1127.9	1134.3	2.8830	0.0012645	1121.1	1133.7	2.8699
280					0.0013216	1220.9	1234.1	3.0548
300					0.0013972	1328.4	1342.3	3.2469
320								
340								

At pressures below 5 MPa for water, the data are approximately equal to the saturated liquid data at the given **temperature**. We approximate intensive parameter  $y$ , that is  $v$ ,  $u$ ,  $h$ , and  $s$  data as

$$y \cong y_f @ T$$

The enthalpy is more sensitive to variations in pressure; therefore, at high pressures the enthalpy can be approximated by

$$h \cong h_{f@T} + v_f (P - P_{sat})$$

For our work, the compressed liquid enthalpy may be approximated by

$$h \cong h_{f@T}$$

### **Saturated Ice-Water Vapor Table**

When the temperature of a substance is below the triple point temperature, the saturated solid and liquid phases exist in equilibrium. Here we define the quality as the ratio of the mass that is vapor to the total mass of solid and vapor in the saturated solid-vapor mixture. The process of changing directly from the solid phase to the vapor phase is called sublimation. Data for saturated ice and water vapor are given in Table A-8. In Table A-8, the term **Subl.** refers to the difference between the saturated vapor value and the saturated solid value.

**TABLE A-8**

Saturated ice—water vapor

Temp., T°C	Sat. press., P <sub>sat</sub> kPa	Specific volume, m <sup>3</sup> /kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/(kg · K)		
		Sat. ice, v <sub>i</sub> × 10 <sup>3</sup>	Sat. vapor, v <sub>g</sub>	Sat. ice, u <sub>i</sub>	Subl., u <sub>ig</sub>	Sat. vapor, u <sub>g</sub>	Sat. ice, h <sub>i</sub>	Subl., h <sub>ig</sub>	Sat. vapor, h <sub>g</sub>	Sat. ice, s <sub>i</sub>	Subl., s <sub>ig</sub>	Sat. vapor, s <sub>g</sub>
0.01	0.6113	1.0908	206.1	-333.40	2708.7	2375.3	-333.40	2834.8	2501.4	-1.221	10.378	9.156
0	0.6108	1.0908	206.3	-333.43	2708.8	2375.3	-333.43	2834.8	2501.3	-1.221	10.378	9.157
-2	0.5176	1.0904	241.7	-337.62	2710.2	2372.6	-337.62	2835.3	2497.7	-1.237	10.456	9.219
-4	0.4375	1.0901	283.8	-341.78	2711.6	2369.8	-341.78	2835.7	2494.0	-1.253	10.536	9.283
-6	0.3689	1.0898	334.2	-345.91	2712.9	2367.0	-345.91	2836.2	2490.3	-1.268	10.616	9.348
-8	0.3102	1.0894	394.4	-350.02	2714.2	2364.2	-350.02	2836.6	2486.6	-1.284	10.698	9.414
-10	0.2602	1.0891	466.7	-354.09	2715.5	2361.4	-354.09	2837.0	2482.9	-1.299	10.781	9.481
-12	0.2176	1.0888	553.7	-358.14	2716.8	2358.7	-358.14	2837.3	2479.2	-1.315	10.865	9.550
-14	0.1815	1.0884	658.8	-362.15	2718.0	2355.9	-362.15	2837.6	2475.5	-1.331	10.950	9.619
-16	0.1510	1.0881	786.0	-366.14	2719.2	2353.1	-366.14	2837.9	2471.8	-1.346	11.036	9.690
-18	0.1252	1.0878	940.5	-370.10	2720.4	2350.3	-370.10	2838.2	2468.1	-1.362	11.123	9.762
-20	0.1035	1.0874	1128.6	-374.03	2721.6	2347.5	-374.03	2838.4	2464.3	-1.377	11.212	9.835
-22	0.0853	1.0871	1358.4	-377.93	2722.7	2344.7	-377.93	2838.6	2460.6	-1.393	11.302	9.909
-24	0.0701	1.0868	1640.1	-381.80	2723.7	2342.0	-381.80	2838.7	2456.9	-1.408	11.394	9.985
-26	0.0574	1.0864	1986.4	-385.64	2724.8	2339.2	-385.64	2838.9	2453.2	-1.424	11.486	10.062
-28	0.0469	1.0861	2413.7	-389.45	2725.8	2336.4	-389.45	2839.0	2449.5	-1.439	11.580	10.141
-30	0.0381	1.0858	2943	-393.23	2726.8	2333.6	-393.23	2839.0	2445.8	-1.455	11.676	10.221
-32	0.0309	1.0854	3600	-396.98	2727.8	2330.8	-396.98	2839.1	2442.1	-1.471	11.773	10.303
-34	0.0250	1.0851	4419	-400.71	2728.7	2328.0	-400.71	2839.1	2438.4	-1.486	11.872	10.386
-36	0.0201	1.0848	5444	-404.40	2729.6	2325.2	-404.40	2839.1	2434.7	-1.501	11.972	10.470
-38	0.0161	1.0844	6731	-408.06	2730.5	2322.4	-408.06	2839.0	2430.9	-1.517	12.073	10.556
-40	0.0129	1.0841	8354	-411.70	2731.3	2319.6	-411.70	2839.9	2427.2	-1.532	12.176	10.644

The specific volume, internal energy, enthalpy, and entropy for a mixture of saturated ice and saturated vapor are calculated similarly to that of saturated liquid-vapor mixtures.

$$y_{ig} = y_g - y_i$$

$$y = y_i + x y_{ig}$$

where the quality  $x$  of a saturated ice-vapor state is

$$x = \frac{m_g}{m_i + m_g}$$

## How to Choose the Right Table

The correct table to use to find the thermodynamic properties of a real substance can always be determined by comparing the known state properties to the properties in the saturation region. Given the temperature or pressure and one other property from the group  $v$ ,  $u$ ,  $h$ , and  $s$ , the following procedure is used. For example if the pressure and specific volume are specified, three questions are asked: For the given pressure,

$$\text{Is } v < v_f ?$$

$$\text{Is } v_f < v < v_g ?$$

$$\text{Is } v_g < v ?$$

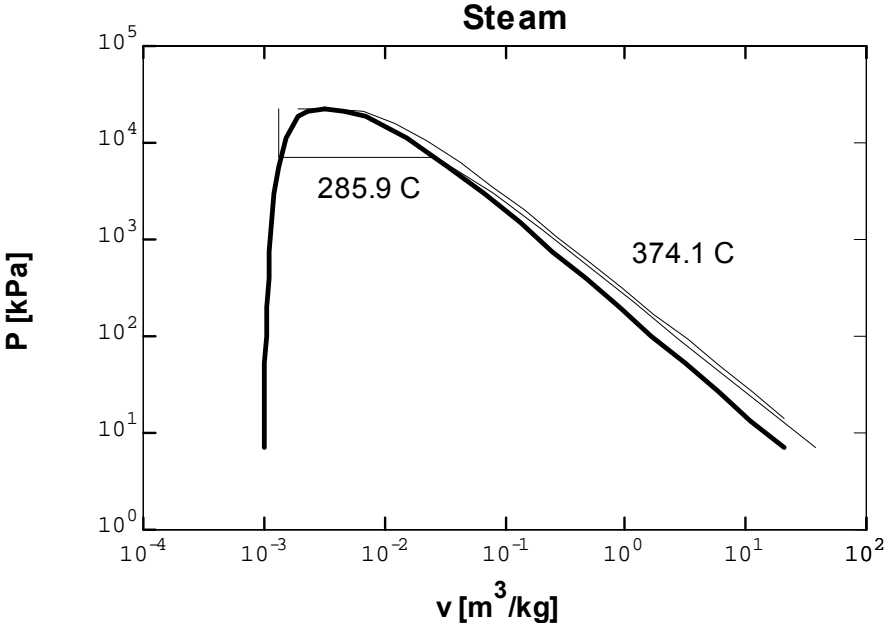
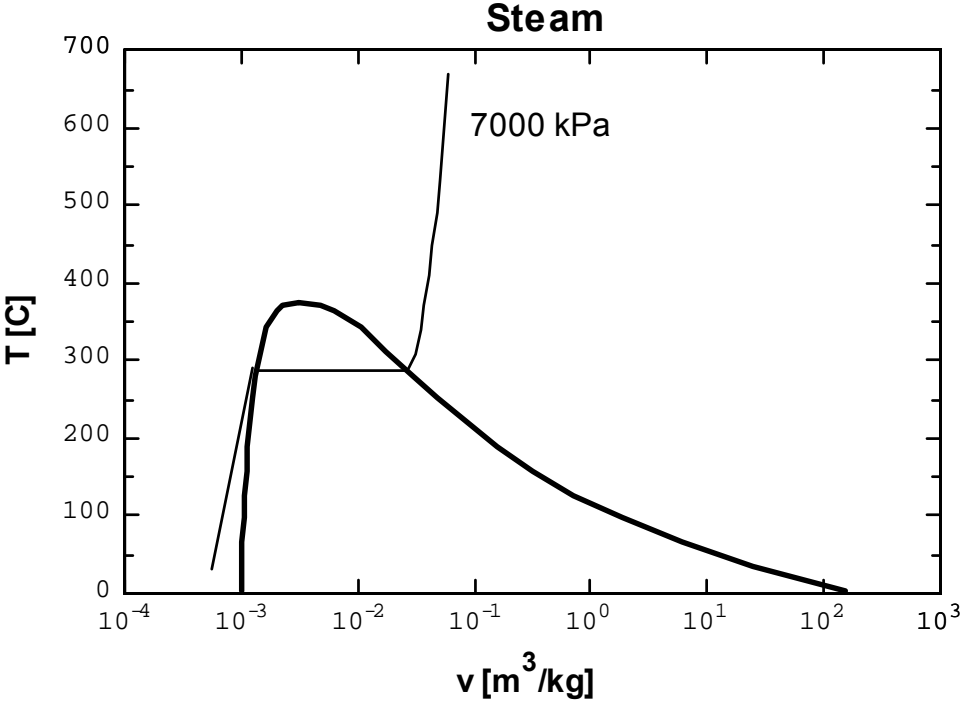
The answer to one of these questions must be yes. If the answer to the first question is yes, the state is in the compressed liquid region, and the compressed liquid tables are used to find the properties of the state. If the answer to the second question is yes, the state is in the saturation region, and either the saturation temperature table or the saturation pressure table is used to find the properties. Then the quality is calculated and is used to calculate the other properties,  $u$ ,  $h$ , and  $s$ . If the answer to the third question is yes, the state is in the superheated region and the superheated tables are used to find the other properties.

Some tables may not always give the internal energy. When it is not listed, the internal energy is calculated from the definition of the enthalpy as

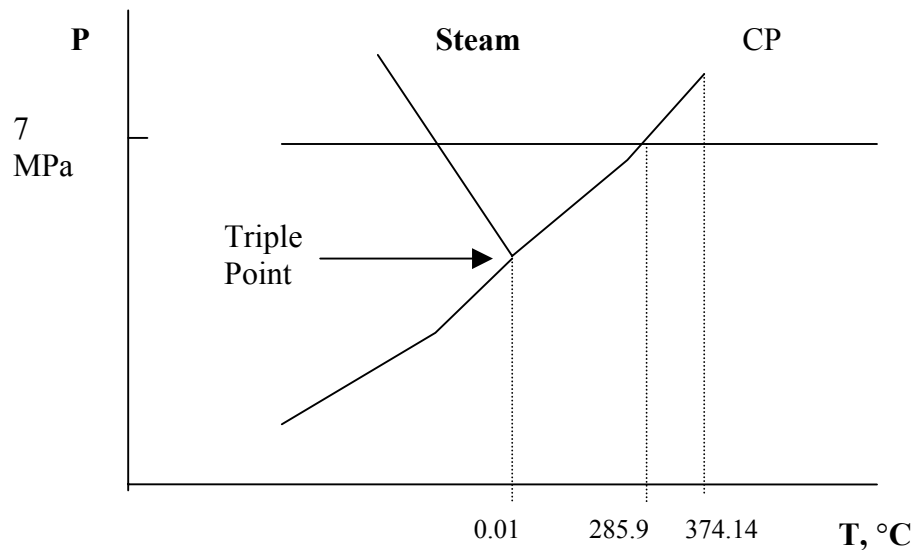
$$u = h - Pv$$

**Example 2-1**

Find the internal energy of water at the given states for 7 MPa and plot the states on  $T$ - $v$ ,  $P$ - $v$ , and  $P$ - $T$  diagrams.







1.  $P = 7$  MPa, dry saturated or saturated vapor

Using Table A-5,

$$u = u_g = 2580.5 \frac{\text{kJ}}{\text{kg}}$$

Locate state 1 on the  $T$ - $v$ ,  $P$ - $v$ , and  $P$ - $T$  diagrams.

2.  $P = 7$  MPa, wet saturated or saturated liquid

Using Table A-5,

$$u = u_f = 1257.6 \frac{\text{kJ}}{\text{kg}}$$

Locate state 2 on the  $T$ - $v$ ,  $P$ - $v$ , and  $P$ - $T$  diagrams.

3. Moisture = 5%,  $P = 7$  MPa

let moisture be  $y$ , defined as

$$y = \frac{m_f}{m} = 0.05$$

then, the quality is

$$x = 1 - y = 1 - 0.05 = 0.95$$

and using Table A-5,

$$\begin{aligned}u &= u_f + x(u_g - u_f) \\&= 1257.6 + 0.95(2580.5 - 1257.6) \\&= 2514.4 \frac{\text{kJ}}{\text{kg}}\end{aligned}$$

Notice that we could have used

$$u = u_f + x u_{fg}$$

Locate state 3 on the  $T$ - $v$ ,  $P$ - $v$ , and  $P$ - $T$  diagrams.

4.  $P = 7 \text{ MPa}$ ,  $T = 600^\circ\text{C}$

For  $P = 7 \text{ MPa}$ , Table A-5 gives  $T_{\text{sat}} = 285.9^\circ\text{C}$ . Since  $600^\circ\text{C} > T_{\text{sat}}$  for this pressure, the state is superheated. Use Table A-6.

$$u = 3260.7 \frac{\text{kJ}}{\text{kg}}$$

Locate state 4 on the  $T$ - $v$ ,  $P$ - $v$ , and  $P$ - $T$  diagrams.

5.  $P = 7 \text{ MPa}$ ,  $T = 100^\circ\text{C}$

Using Table A-4, At  $T = 100^\circ\text{C}$ ,  $P_{\text{sat}} = 0.10132 \text{ MPa}$ . Since  $P > P_{\text{sat}}$ , the state is compressed liquid.

Approximate solution:

$$u \cong u_{f@T=100C} = 418.94 \frac{kJ}{kg}$$

Solution using Table A-7:

We do linear interpolation to get the value at 100 °C. (We will demonstrate how to do linear interpolation with this problem even though one could accurately estimate the answer.)

$P$ MPa	$u$ kJ/kg
5	417.52
7	$u = ?$
10	416.12

The interpolation scheme is called “the ratio of corresponding differences.”

Using the above table, form the following ratios.

$$\frac{5 - 7}{5 - 10} = \frac{417.52 - u}{417.52 - 416.12}$$
$$u = 416.96 \frac{kJ}{kg}$$

Locate state 5 on the  $T$ - $v$ ,  $P$ - $v$ , and  $P$ - $T$  diagrams.

6.  $P = 7$  MPa,  $T = 460^\circ\text{C}$

Since  $460^\circ\text{C} > T_{\text{sat}}$  at  $P = 7$  MPa, the state is superheated. Using Table A-6, we do linear interpolation to get  $u$ .

T °C	u kJ/kg
450	2978.0
460	u = ?
500	3073.4

Using the above table, form the following ratios.

$$\frac{460 - 450}{500 - 450} = \frac{u - 2978.0}{3073.4 - 2978.0}$$

$$u = 2997.1 \frac{\text{kJ}}{\text{kg}}$$

Locate state 6 on the  $T$ - $v$ ,  $P$ - $v$ , and  $P$ - $T$  diagrams.

### Example 2-2

Determine the enthalpy of 1.5 kg of water contained in a volume of 1.2 m<sup>3</sup> at 200 kPa.

Recall we need two independent, intensive properties to specify the state of a simple substance. Pressure  $P$  is one intensive property and specific volume is another. Therefore, we calculate the specific volume.

$$v = \frac{\text{Volume}}{\text{mass}} = \frac{1.2 \text{ m}^3}{1.5 \text{ kg}} = 0.8 \frac{\text{m}^3}{\text{kg}}$$

Using Table A-5 at  $P = 200$  kPa,

$$v_f = 0.001061 \text{ m}^3/\text{kg}, \quad v_g = 0.8857 \text{ m}^3/\text{kg}$$

Now,

Is  $v < v_f$  ? No

Is  $v_f < v < v_g$  ? Yes

Is  $v_g < v$  ? No

Locate this state on a  $T$ - $v$  diagram.



We see that the state is in the two-phase or saturation region. So we must find the quality  $x$  first.

$$v = v_f + x(v_g - v_f)$$

$$\begin{aligned} x &= \frac{v - v_f}{v_g - v_f} \\ &= \frac{0.8 - 0.001061}{0.8857 - 0.001061} \\ &= 0.903 \quad (\text{What does this mean?}) \end{aligned}$$

Then,

$$\begin{aligned} h &= h_f + x h_{fg} \\ &= 504.7 + (0.903)(2201.9) \\ &= 2493.3 \frac{kJ}{kg} \end{aligned}$$

### Example 2-3

Determine the internal energy of refrigerant-134a at a temperature of 0°C and a quality of 60%.

Using Table A-11, for  $T = 0^\circ\text{C}$ ,

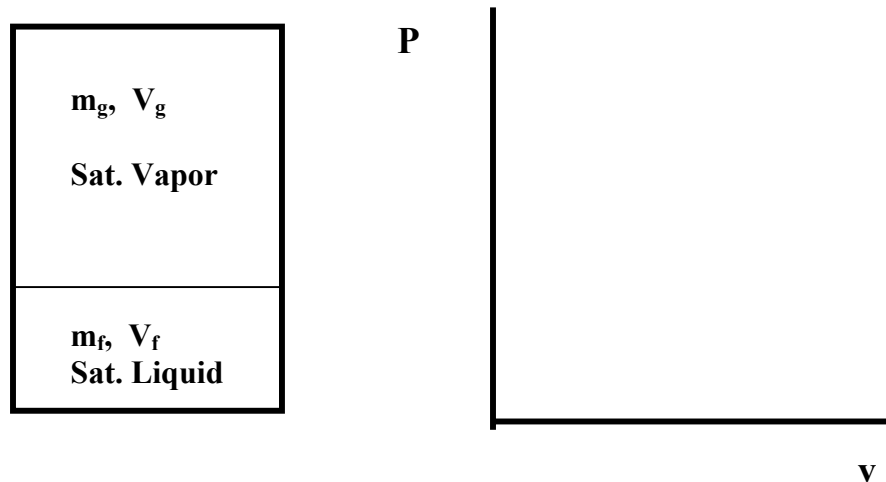
$$u_f = 49.79 \text{ kJ/kg} \quad u_g = 227.06 \text{ kJ/kg}$$

then,

$$\begin{aligned} u &= u_f + x(u_g - u_f) \\ &= 49.79 + (0.6)(227.06 - 49.79) \\ &= 156.15 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

### Example 2-4

Consider the closed, rigid container of water shown below. The pressure is 700 kPa, the mass of the saturated liquid is 1.78 kg, and the mass of the saturated vapor is 0.22 kg. Heat is added to the water until the pressure increases to 8 MPa. Find the final temperature, enthalpy, and internal energy of the water. Does the liquid level rise or fall? Plot this process on a  $P$ - $v$  diagram with respect to the saturation lines and the critical point.



Let's introduce a solution procedure that we will follow throughout the course. This solution technique is discussed in detail in Chapter 3.

**System:** A closed system composed of the water enclosed in the tank

**Property Relation:** Steam Tables

**Process:** Volume is constant (rigid container)

For the closed system the total mass is constant and since the process is one in which the volume is constant, the average specific volume of the saturated mixture during the process is given by

$$v = \frac{V}{m} = \text{constant}$$

or

$$v_2 = v_1$$

Now to find  $v_1$  recall that in the two-phase region at state 1

$$x_1 = \frac{m_{g1}}{m_{f1} + m_{g1}} = \frac{0.22 \text{ kg}}{(1.78 + 0.22) \text{ kg}} = 0.11$$

Then, at  $P = 700 \text{ kPa}$

$$\begin{aligned} v_1 &= v_{f1} + x_1 (v_{g1} - v_{f1}) \\ &= 0.001108 + (0.11)(0.2729 - 0.001108) \\ &= 0.031 \frac{m^3}{kg} \end{aligned}$$

State 2 is specified by:

$$P_2 = 8 \text{ MPa}, \quad v_2 = 0.031 \text{ m}^3/\text{kg}$$

At 8 MPa,

$$v_f = 0.001384 \text{ m}^3/\text{kg} \quad v_g = 0.002352 \text{ m}^3/\text{kg}$$

at 8 MPa,  $v_2 = 0.031 \text{ m}^3/\text{kg}$ ; therefore, is

Is  $v_2 < v_f$  ? No

Is  $v_f < v_2 < v_g$  ? No

Is  $v_g < v_2$  ? Yes

Therefore, State 2 is superheated.

Interpolating in the superheated tables at 8 MPa gives,

$$\begin{aligned} T_2 &= 362 \text{ }^\circ\text{C} \\ h_2 &= 3024 \text{ kJ/kg} \\ u_2 &= 2776 \text{ kJ/kg} \end{aligned}$$

Since state 2 is superheated, the liquid level falls.

### **Extra Problem**

What would happen to the liquid level in the last example if the specific volume had been  $0.001 \text{ m}^3/\text{kg}$  and the pressure was 8 MPa?



### Extra Assignment

Complete the following table for properties of water

Sketch a  $T$ - $v$  or  $P$ - $v$  diagram for each state. Describe the phase as compressed liquid, saturated mixture, or superheated vapor. If the state is saturated mixture, give the quality.

$P$ MPa	$v$ $m^3/kg$	$T$ $^{\circ}C$	Phase Description and Quality if Applicable
	1.725	100	
0.85	0.227		
15.0		400	
	0.001124	180	
0.75	0.221		
	0.3879	150	
0.25	0.095		
	0.04	350	
20.0		300	
1.6	0.2		
3.5	0.095		
10.0		220	
	0.580	135	
	0.055	500	
0.4	0.4625		

## Equations of State

The relationship among the state variables, temperature, pressure, and specific volume is called the equation of state. We now consider the equation of state for the vapor or gaseous phase of simple compressible substances.

$$F(P, T, \nu) \equiv 0$$

## Ideal Gas

Based on our experience in chemistry and physics we recall that the combination of Boyle's and Charles' laws for gases at low pressure result in the equation of state for the ideal gas as

$$P = R \left( \frac{T}{\nu} \right)$$

where  $R$  is the constant of proportionality and is called the **gas constant** and takes on a different value for each gas. If a gas obeys this relation, it is called an ideal gas. We often write this equation as

$$P\nu = RT$$

The gas constant for ideal gases is related to the universal gas constant valid for all substances through the molar mass (or molecular weight). Let  $R_u$  be the universal gas constant. Then,

$$R = \frac{R_u}{M}$$

The mass,  $m$ , is related to the moles,  $N$ , of substance through the molecular weight or molar mass,  $\mathbf{M}$ , see Table A-1. The molar mass is the ratio of mass to moles and has the same value regardless of the system of units.

$$M_{air} = 28.97 \frac{g}{gmol} = 28.97 \frac{kg}{kmol} = 28.97 \frac{lbm}{lbmol}$$

Since 1 kmol = 1000 gmol or 1000 gram-mole and 1 kg = 1000 g, 1 kmol of air has a mass of 28.97 kg or 28,970 grams.

$$m = N M$$

The ideal gas equation of state may be written several ways.

$$Pv = RT$$

$$P \frac{V}{m} = RT$$

$$PV = mRT$$

$$PV = \frac{m}{M} (MR)T$$

$$PV = NR_u T$$

$$P \frac{V}{N} = R_u T$$

$$P\bar{v} = R_u T$$

Here

$P =$  **absolute pressure** in MPa, or kPa

$\bar{v} =$  molar specific volume in  $\text{m}^3/\text{kmol}$

$T =$  **absolute temperature** in K

$R_u = 8.314 \text{ kJ}/(\text{kmol}\cdot\text{K})$

Some values of the universal gas constant are

Universal Gas Constant,  $R_u$

8.314 kJ/(kmol·K)

8.314 kPa·m<sup>3</sup>/(kmol·K)

1.986 Btu/(lbmol·R)

1545 ft·lbf/(lbmol·R)

10.73 psia·ft<sup>3</sup>/(lbmol·R)

The ideal gas equation of state can be derived from basic principles if one assumes

1. Intermolecular forces are small.
2. Volume occupied by the particles is small.

### Example 2-5

Determine the particular gas constant for air and hydrogen.

$$R = \frac{R_u}{M}$$

$$R_{air} = \frac{8.314 \frac{\text{kJ}}{\text{kmol}\cdot\text{K}}}{28.97 \frac{\text{kg}}{\text{kmol}}} = 0.287 \frac{\text{kJ}}{\text{kg}\cdot\text{K}}$$

$$R_{hydrogen} = \frac{8.314 \frac{kJ}{kmol - K}}{2.016 \frac{kg}{kmol}} = 4.124 \frac{kJ}{kg - K}$$

The ideal gas equation of state is used when (1) the pressure is small compared to the critical pressure or (2) when the temperature is twice the critical temperature and the pressure is less than 10 times the critical pressure. The critical point is that state where there is an instantaneous change from the liquid phase to the vapor phase for a substance. Critical point data are given in Table A-1.

### Compressibility Factor

To understand the above criteria and to determine how much the ideal gas equation of state deviates from the actual gas behavior, we introduce the compressibility factor  $Z$  as follows.

$$P\bar{v} = Z R_u T$$

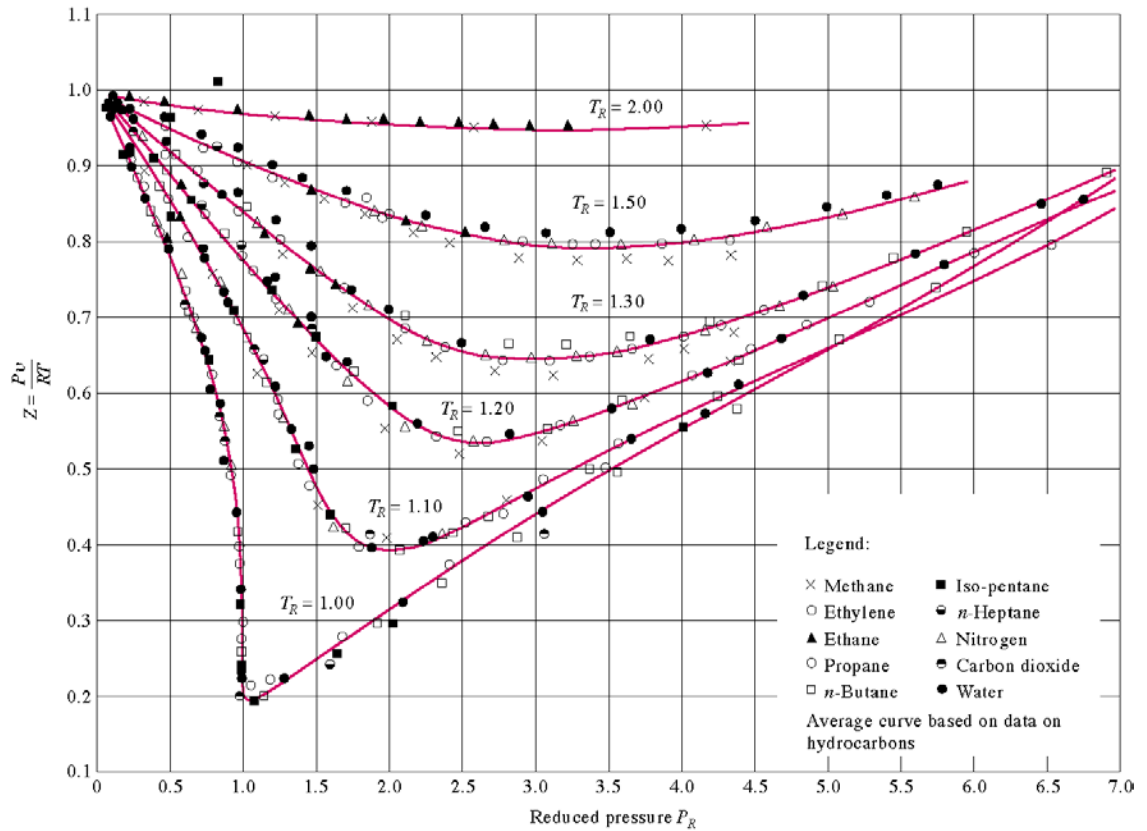
or

$$Z = \frac{P\bar{v}}{R_u T}$$

For an ideal gas  $Z = 1$ , and the deviation of  $Z$  from unity measures the deviation of the actual  $P$ - $V$ - $T$  relation from the ideal gas equation of state. The compressibility factor is expressed as a function of the reduced pressure and the reduced temperature. The  $Z$  factor is approximately the same for all gases at the same *reduced temperature* and *reduced pressure*, which are defined as

$$T_R = \frac{T}{T_{cr}} \quad \text{and} \quad P_R = \frac{P}{P_{cr}}$$

where  $P_{cr}$  and  $T_{cr}$  are the critical pressure and temperature, respectively. The critical constant data for various substances are given in Table A-1. This is known as the *principle of corresponding states*. Figure 2-51 gives a comparison of  $Z$  factors for various gases and supports the principle of corresponding states.



When either  $P$  or  $T$  is unknown,  $Z$  can be determined from the compressibility chart with the help of the *pseudo-reduced specific volume*, defined as

$$v_R = \frac{v_{actual}}{\frac{RT_{cr}}{P_{cr}}}$$

Figure A-30 presents the generalized compressibility chart based on data for a large number of gases.

These charts show the conditions for which  $Z = 1$  and the gas behaves as an ideal gas:

1.  $P_R < 10$  and  $T_R > 2$  or  $P < 10P_{cr}$  and  $T > 2T_{cr}$
2.  $P_R \ll 1$  or  $P \ll P_{cr}$

Note: When  $P_R$  is small, we must make sure that the state is not in the compressed liquid region for the given temperature. A compressed liquid state is certainly not an ideal gas state.

For instance the critical pressure and temperature for oxygen are 5.08 MPa and 154.8 K, respectively. For temperatures greater than 300 K and pressures less than 50 MPa (1 atmosphere pressure is 0.10135 MPa) oxygen is considered to be an ideal gas.

### Example 2-6

Calculate the specific volume of nitrogen at 300 K and 8.0 Mpa and compare the result with the value given in a nitrogen table as  $v = 0.011133 \text{ m}^3/\text{kg}$ .

From Table A.1 for nitrogen

$$T_{cr} = 126.2 \text{ K}, P_{cr} = 3.39 \text{ MPa} \quad R = 0.2968 \text{ kJ/kg-K}$$

$$T_R = \frac{T}{T_{cr}} = \frac{300\text{K}}{126.2\text{K}} = 2.38$$

$$P_R = \frac{P}{P_{cr}} = \frac{8.0\text{MPa}}{3.39\text{MPa}} = 2.36$$

Since  $T > 2T_{cr}$  and  $P < 10P_{cr}$ , we use the ideal gas equation of state

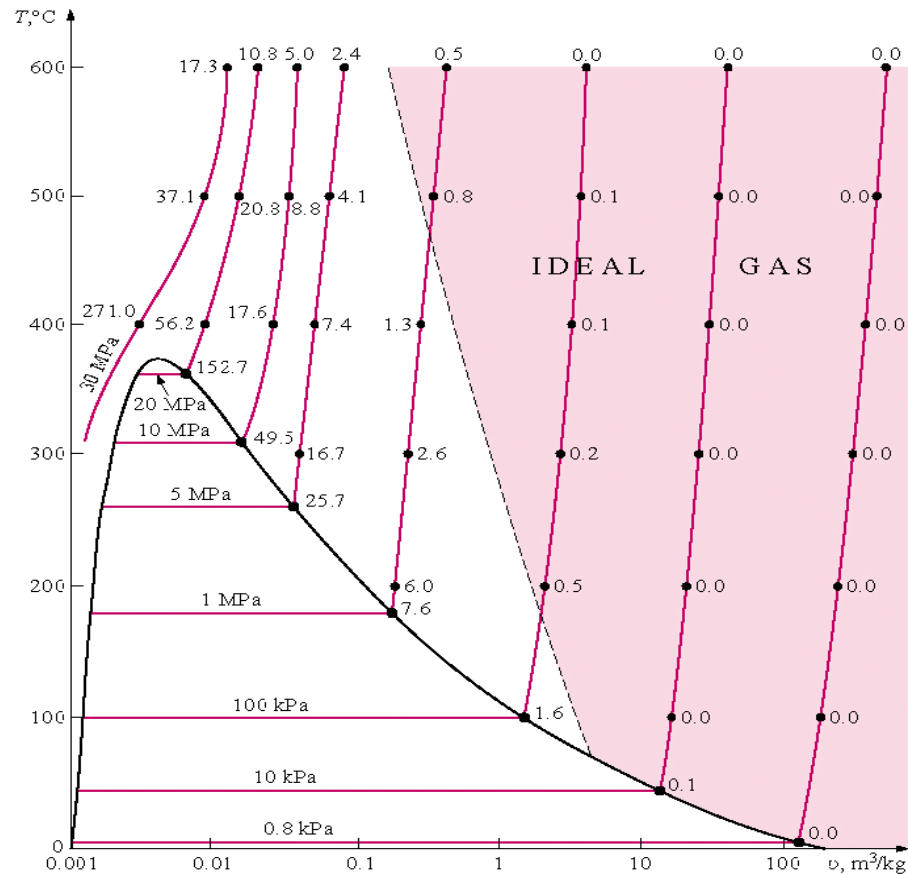
$$Pv = RT$$

$$\begin{aligned} v &= \frac{RT}{P} = \frac{0.2968 \frac{\text{kJ}}{\text{kg-K}} (300\text{K})}{8.0\text{MPa}} \frac{\text{m}^3 \text{MPa}}{10^3 \text{kJ}} \\ &= 0.01113 \frac{\text{m}^3}{\text{kg}} \end{aligned}$$



Nitrogen is clearly an ideal gas at this state.

If the system pressure is low enough and the temperature high enough ( $P$  and  $T$  are compared to the critical values), gases will behave as ideal gases. Consider the  $T$ - $v$  diagram for water. The figure below shows the percentage of error for the volume ( $[|v_{\text{table}} - v_{\text{ideal}}|/v_{\text{table}}] \times 100$ ) for assuming water (superheated steam) to be an ideal gas.



We see that the region for which water behaves as an ideal gas is in the superheated region and depends on both  $T$  and  $P$ . We must be cautioned that in this course, when water is the working fluid, the ideal gas assumption may not be used to solve problems. We must use the real gas relations, i.e., the property tables.

### Useful Ideal Gas Relation: The Combined Gas Law

By writing the ideal gas equation twice for a fixed mass and simplifying, the properties of an ideal gas at two different states are related by

$$m_1 = m_2$$

or

$$\frac{P_1 V_1}{R T_1} = \frac{P_2 V_2}{R T_2}$$

But, the gas constant is \_\_\_\_\_(fill in the blank), so

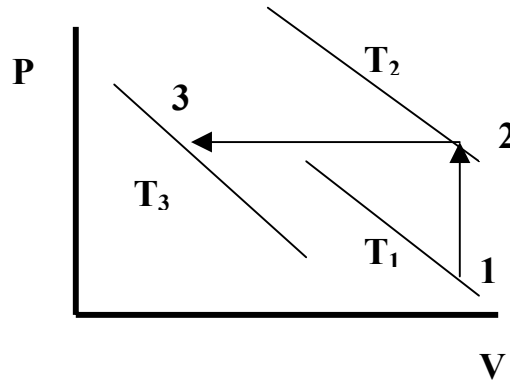
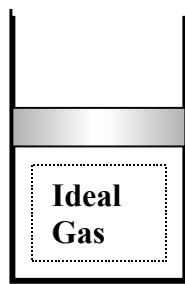
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

### **Example 2-7**

An ideal gas having an initial temperature of 25 °C under goes the two processes described below. Determine the final temperature of the gas.

Process 1-2: The volume is held constant while the pressure doubles.

Process 2-3: The pressure is held constant while the volume is reduced to one-third of the original volume.



Process 1-3:

$$m_1 = m_3$$

or

$$\frac{P_1 V_1}{T_1} = \frac{P_3 V_3}{T_3}$$

but  $V_3 = V_1/3$  and  $P_3 = P_2 = 2P_1$

Therefore,

$$\begin{aligned} T_3 &= T_1 \frac{P_3 V_3}{P_1 V_1} \\ &= T_1 \frac{2P_1 V_1 / 3}{P_1 V_1} = \frac{2}{3} T_1 \end{aligned}$$

$$T_3 = \frac{2}{3} (25 + 273) K = 198.7 K = -74.3^\circ C$$

### Other Equations of State

Many attempts have been made to keep the simplicity of the ideal gas equation of state but yet account for the intermolecular forces and volume occupied by the particles. Three of these are

*van der Waals:*

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

where

$$a = \frac{27R^2T_{cr}^2}{64P_{cr}} \quad \text{and} \quad b = \frac{RT_{cr}}{8P_{cr}}$$

### Extra Assignment

When plotted on the  $P$ - $v$  diagram, the critical isotherm has a point of inflection at the critical point. Use this information to verify the equations for van der Waals' constants  $a$  and  $b$ .

*Beattie-Bridgeman:*

$$P = \frac{R_u T}{\bar{v}^2} \left(1 - \frac{c}{\bar{v} T^3}\right) (\bar{v} + B) - \frac{A}{\bar{v}^2}$$

where

$$A = A_o \left(1 - \frac{a}{\bar{v}}\right) \quad \text{and} \quad B = B_o \left(1 - \frac{b}{\bar{v}}\right)$$

The constants  $a$ ,  $b$ ,  $c$ ,  $A_o$ ,  $B_o$  for various substances are found in Table 2-4.

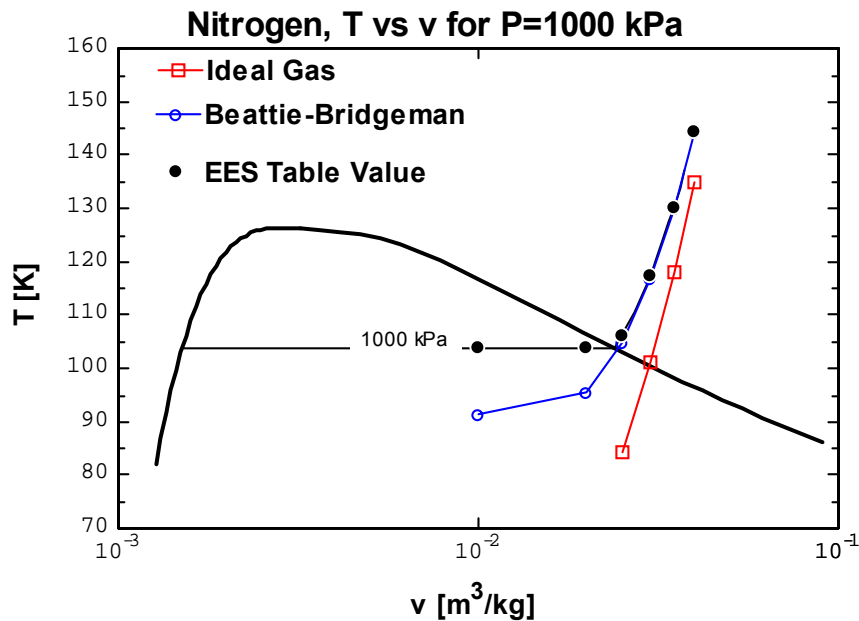
*Benedict-Webb-Rubin:*

$$P = \frac{R_u T}{\bar{v}} + \left( B_o R_u T - A_o - \frac{C_o}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2} \left( 1 + \frac{\gamma}{\bar{v}^2} \right) e^{-\gamma/\bar{v}^2}$$

The constants for various substances appearing in the Benedict-Webb-Rubin equation are given in Table 2-4.

## Example 2-8

Problem 2-95 at the end of Chapter 2 asks for the comparison of the ideal gas equation and the Beattie-Bridgeman equation for nitrogen at 1000 kPa. The following is an EES solution to that problem. See the solution given on the software disk.



Notice that the results from the Beattie-Bridgeman equation compare well in the gaseous or superheated region with the actual nitrogen data provided by EES. However, neither the Beattie-Bridgeman equation nor the ideal gas equation provides adequate results in the two-phase region, where the gas (ideal or otherwise) assumption fails.

## Specific Heats, Changes in Internal Energy and Enthalpy for Ideal Gases

Before the first law of thermodynamics can be applied to systems, ways to calculate the change in internal energy of the substance enclosed by the system boundary must be determined. For real substances like water, the property tables are used to find the internal energy change. For ideal gases the internal energy is found by knowing the specific heats. Physics defines the amount of energy needed to raise the temperature of a unit of mass of a substance one degree as the specific heat at constant volume  $C_V$  for a constant-volume process, and the specific heat at constant pressure  $C_P$  for a constant-pressure process. Recall that enthalpy  $h$  is the sum of the internal energy  $u$  and the pressure-volume product  $Pv$ .

$$h = u + Pv$$

In thermodynamics, the specific heats are defined as

$$C_V = \left( \frac{\partial u}{\partial T} \right)_v \quad \text{and} \quad C_P = \left( \frac{\partial h}{\partial T} \right)_P$$

### Simple Substance

The thermodynamic state of a simple, homogeneous substance is specified by giving any two independent, intensive properties. Let's consider the internal energy to be a function of  $T$  and  $v$  and the enthalpy to be a function of  $T$  and  $P$  as follows:

$$u = u(T, v) \quad \text{and} \quad h = h(T, P)$$

The total differential of  $u$  is

$$du = \left( \frac{\partial u}{\partial T} \right)_v dT + \left( \frac{\partial u}{\partial v} \right)_T dv$$

*or*

$$du = C_v dT + \left( \frac{\partial u}{\partial v} \right)_T dv$$

The total differential of  $h$  is

$$dh = \left( \frac{\partial h}{\partial T} \right)_P dT + \left( \frac{\partial h}{\partial P} \right)_T dP$$

*or*

$$dh = C_P dT + \left( \frac{\partial h}{\partial P} \right)_T dP$$

Using thermodynamic relation theory, we could evaluate the remaining partial derivatives of  $u$  and  $h$  in terms of functions of  $P, v$ , and  $T$ . These functions depend upon the equation of state for the substance. Given the specific heat data and the equation of state for the substance, we can develop the property tables like the steam tables.

### **Ideal Gases**

For ideal gases, we use thermodynamic function relation theory of Chapter 11 and the equation of state ( $Pv = RT$ ) to show that  $u$ ,  $h$ ,  $C_v$ , and  $C_P$  are functions of temperature alone. Then for ideal gases,



$$C_V = C_V(T) \quad \text{and} \quad \left( \frac{\partial u}{\partial v} \right)_T \equiv 0$$

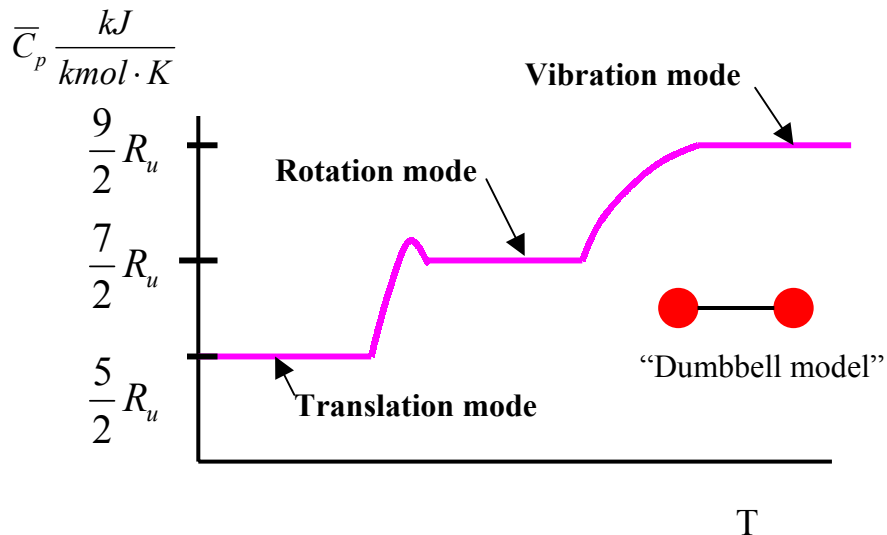
$$C_P = C_P(T) \quad \text{and} \quad \left( \frac{\partial h}{\partial P} \right)_T \equiv 0$$

The ideal gas specific heats are written in terms of ordinary differentials as

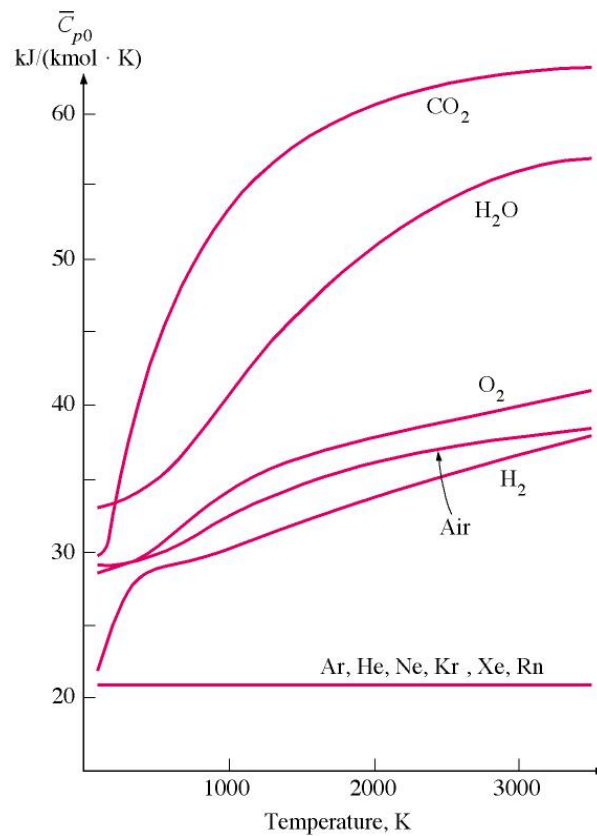
$$C_V = \left( \frac{du}{dT} \right)_{ideal\ gas}$$

$$C_P = \left( \frac{dh}{dT} \right)_{ideal\ gas}$$

Using the simple “dumbbell model” for diatomic ideal gases, statistical thermodynamics predicts the molar specific heat at constant pressure as a function of temperature to look like the following



The following figure shows how the molar specific heats vary with temperature for selected ideal gases.



The differential changes in internal energy and enthalpy for ideal gases become

$$du = C_V dT$$

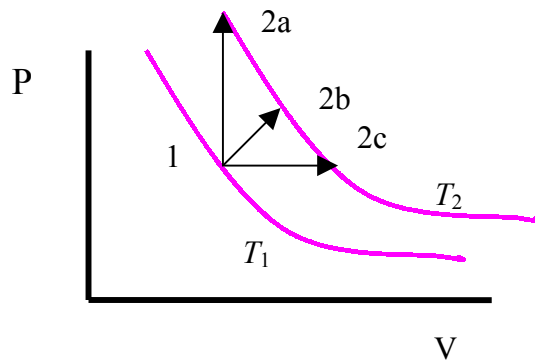
$$dh = C_P dT$$

The change in internal energy and enthalpy of ideal gases can be expressed as

$$\Delta u = u_2 - u_1 = \int_1^2 C_V(T) dT = C_{V,ave}(T_2 - T_1)$$

$$\Delta h = h_2 - h_1 = \int_1^2 C_P(T) dT = C_{P,ave}(T_2 - T_1)$$

where  $C_{V,ave}$  and  $C_{P,ave}$  are average or constant values of the specific heats over the temperature range. We will drop the **ave** subscript shortly.



***P-V* diagram for several processes for an ideal**

In the above figure an ideal gas undergoes three different process between the same two temperatures.

Process 1-2a: Constant volume

Process 1-2b:  $P = a + bV$ , a linear relationship

Process 1-2c: Constant pressure

These ideal gas processes have the same change in internal energy and enthalpy because the processes occur between the same temperature limits.

$$\Delta u_a = \Delta u_b = \Delta u_c = \int_1^2 C_V(T) dT$$

$$\Delta h_a = \Delta h_b = \Delta h_c = \int_1^2 C_P(T) dT$$

To find  $\Delta u$  and  $\Delta h$  we often use average, or constant, values of the specific heats. Some ways to determine these values are as follows:

1. The best average value (the one that gives the exact results)

See Table A-2c for variable specific data.

$$C_{v,ave} = \frac{\int_1^2 C_V(T) dT}{T_2 - T_1} \quad \text{and} \quad C_{P,ave} = \frac{\int_1^2 C_P(T) dT}{T_2 - T_1}$$

2. Good average values are

$$C_{v,ave} = \frac{C_V(T_2) + C_V(T_1)}{2} \quad \text{and} \quad C_{P,ave} = \frac{C_P(T_2) + C_P(T_1)}{2}$$

and

$$C_{v,ave} = C_V(T_{ave}) \quad \text{and} \quad C_{P,ave} = C_P(T_{ave})$$

where

$$T_{ave} = \frac{T_2 + T_1}{2}$$

3. Sometimes adequate (and most often used) values are the ones evaluated at 300 K and are given in Table A-2(a).

$$C_{v,ave} = C_V(300K) \quad \text{and} \quad C_{P,ave} = C_P(300K)$$

Let's take a second look at the definition of  $\Delta u$  and  $\Delta h$  for ideal gases. Just consider the enthalpy for now.

$$\Delta h = h_2 - h_1 = \int_1^2 C_P(T) dT$$

Let's perform the integral relative to a reference state where  $h = h_{ref}$  at  $T = T_{ref}$ .

$$\Delta h = h_2 - h_1 = \int_{T_1}^{T_{ref}} C_P(T') dT' + \int_{T_{ref}}^{T_2} C_P(T') dT'$$

or

$$\begin{aligned} \Delta h = h_2 - h_1 &= \int_{T_{ref}}^{T_2} C_P(T') dT' - \int_{T_{ref}}^{T_1} C_P(T') dT' \\ &= (h_2 - h_{ref}) - (h_1 - h_{ref}) \end{aligned}$$

At any temperature, we can calculate the enthalpy relative to the reference state as

$$h - h_{ref} = \int_{T_{ref}}^T C_P(T') dT'$$

or

$$h = h_{ref} + \int_{T_{ref}}^T C_P(T') dT'$$

Similarly, the internal energy change relative to the reference state is

$$u - u_{ref} = \int_{T_{ref}}^T C_V(T')dT'$$

or

$$u = u_{ref} + \int_{T_{ref}}^T C_V(T')dT'$$

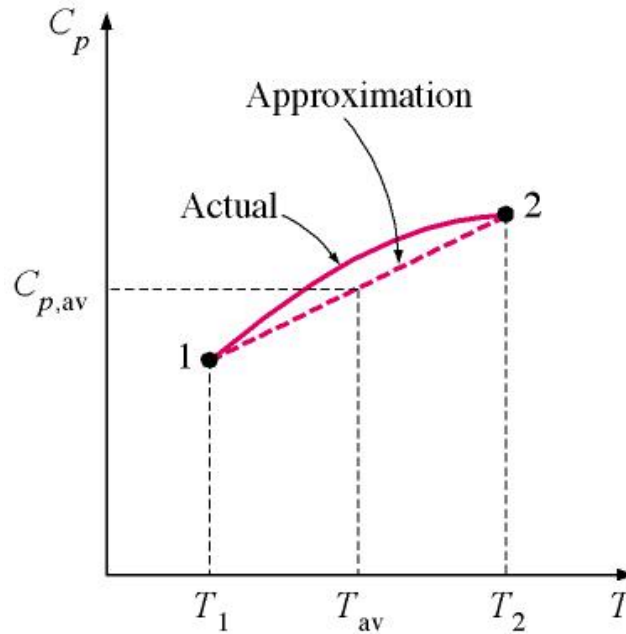
These last two relations form the basis of the air tables (Table A-17 on a mass basis) and the other ideal gas tables (Tables A-18 through A-25 on a mole basis). When you review Table A-17, you will find  $h$  and  $u$  as functions of  $T$  in K. Since the parameters  $P_r$ ,  $v_r$ , and  $s^\circ$ , also found in Table A-17, apply to air only in a particular process, call isentropic, you should ignore these parameters until we study Chapter 6. The reference state for these tables is defined as

$$u_{ref} = 0 \text{ at } T_{ref} = 0K$$

$$h_{ref} = 0 \text{ at } T_{ref} = 0K$$

AIR		
$T, K$	$u, kJ/kg$	$h, kJ/kg$
0	0	0
·	·	·
·	·	·
300	214.17	300.19
310	221.25	310.24
·	·	·
·	·	·

Partial listing of Table A.17 given in Figure 2-69



In the analysis to follow, the “ave” notation is dropped. In most applications for ideal gases, the values of the specific heats at 300 K given in Table A-2 are adequate constants.

### Exercise

Determine the average specific heat for air at 305 K.

$$C_{P,ave} =$$

(Answer: 1.005 kJ/kg·K, approximate the derivative of  $h$  wrt  $T$  as differences)

## Relation between $C_P$ and $C_V$ for Ideal Gases

Using the definition of enthalpy ( $h = u + Pv$ ) and writing the differential of enthalpy, the relationship between the specific heats for ideal gases is

$$h = u + Pv$$

$$dh = du + d(RT)$$

$$C_P dT = C_V dT + R dT$$

$$C_P = C_V + R$$

where  $R$  is the particular gas constant. The specific heat ratio  $k$  (fluids texts often use  $\gamma$  instead of  $k$ ) is defined as

$$k = \frac{C_P}{C_V}$$

### Extra Problem

Show that

$$C_P = \frac{kR}{k-1} \quad \text{and} \quad C_V = \frac{R}{k-1}$$



### Example 2-9

Two kilograms of air are heated from 300 to 500 K. Find the change in enthalpy by assuming

- Empirical specific heat data from Table A-2(c).
- Air tables from Table A-17.
- Specific heat at the average temperature from Table A-2(c).
- Use the 300 K value for the specific heat from Table A-2(a).

a. Table A-2(c) gives the molar specific heat at constant pressure for air as

$$\bar{C}_p = 28.11 + 0.1967 \times 10^{-2} T + 0.4802 \times 10^{-5} T^2 - 1.966 \times 10^{-9} T^3 \quad \frac{kJ}{kmol \cdot K}$$

The enthalpy change per unit mole is

$$\begin{aligned} \Delta \bar{h} &= \bar{h}_2 - \bar{h}_1 = \int_1^2 \bar{C}_p(T) dT \\ &= \int_{300K}^{500K} (28.11 + 0.1967 \times 10^{-2} T + 0.4802 \times 10^{-5} T^2 \\ &\quad - 1.966 \times 10^{-9} T^3) dT \\ &= \left( 28.11T + \frac{0.1967 \times 10^{-2}}{2} T^2 + \frac{0.4802 \times 10^{-5}}{3} T^3 \right. \\ &\quad \left. - \frac{1.966 \times 10^{-9}}{4} T^4 \right)_{300K}^{500K} \\ &= 5909.49 \frac{kJ}{kmol} \end{aligned}$$

$$\Delta h = \frac{\Delta \bar{h}}{M} = \frac{5909.49 \frac{\text{kJ}}{\text{kmol}}}{28.97 \frac{\text{kg}}{\text{kmol}}} = 203.9 \frac{\text{kJ}}{\text{kg}}$$

$$\Delta H = m\Delta h = (2 \text{ kg})(203.9 \frac{\text{kJ}}{\text{kg}}) = 407.98 \text{ kJ}$$

- b. Using the air tables, Table A-17, at  $T_1 = 300 \text{ K}$ ,  $h_1 = 300.19 \text{ kJ/kg}$  and at  $T_2 = 500 \text{ K}$ ,  $h_2 = 503.02 \text{ kJ/kg}$

$$\Delta H = m\Delta h = (2 \text{ kg})(503.02 - 300.19) \frac{\text{kJ}}{\text{kg}} = 405.66 \text{ kJ}$$

The results of parts a and b would be identical if Table A-17 had been based on the same specific heat function listed in Table A-2(c).

- c. Let's use a constant specific heat at the average temperature.

$T_{\text{ave}} = (300 + 500)\text{K}/2 = 400 \text{ K}$ . At  $T_{\text{ave}}$ , Table A-2 gives  $C_p = 1.013 \text{ kJ}/(\text{kg}\cdot\text{K})$ .

For  $C_p = \text{constant}$ ,

$$\begin{aligned}
\Delta h &= h_2 - h_1 = C_{P,ave} (T_2 - T_1) \\
&= 1.013 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} (500 - 300) \text{ K} \\
&= 202.6 \frac{\text{kJ}}{\text{kg}} \\
\Delta H &= m\Delta h = (2 \text{ kg})(202.6) \frac{\text{kJ}}{\text{kg}} = 405.2 \text{ kJ}
\end{aligned}$$

d. Using the 300 K value from Table A-2(a),  $C_p = 1.005 \text{ kJ/kg} \cdot \text{K}$ .

For  $C_p = \text{constant}$ ,

$$\begin{aligned}
\Delta h &= h_2 - h_1 = C_p (T_2 - T_1) \\
&= 1.005 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} (500 - 300) \text{ K} \\
&= 201.0 \frac{\text{kJ}}{\text{kg}} \\
\Delta H &= m\Delta h = (2 \text{ kg})(201.0) \frac{\text{kJ}}{\text{kg}} = 402.0 \text{ kJ}
\end{aligned}$$

### Extra Problem

Find the change in internal energy for air between 300 K and 500 K, in kJ/kg.

## Internal Energy and Enthalpy Changes of Solids and Liquids

We treat solids and liquids as incompressible substances. That is, we assume that the density or specific volume of the substance is essentially constant during a process. We can show that the specific heats of incompressible substances (see Chapter 11) are identical.

$$C_P = C_V = C \quad \left( \frac{kJ}{kg \cdot K} \right)$$

The specific heats of incompressible substances depend only on temperature; therefore, we write the differential change in internal energy as

$$du = C_V dT = C dT$$

and assuming constant specific heats, the change in internal energy is

$$\Delta u = C\Delta T = C(T_2 - T_1)$$

Recall that enthalpy is defined as

$$h = u + Pv$$

The differential of enthalpy is

$$dh = du + Pdv + vdP$$

For incompressible substances, the differential enthalpy becomes

$$dv = 0$$

$$dh = du + Pdv^0 + vdP$$

$$dh = du + vdP$$

Integrating, assuming constant specific heats

$$\Delta h = \Delta u + v\Delta P = C\Delta T + v\Delta P$$

For **solids** the specific volume is approximately zero; therefore,

$$\Delta h_{solid} = \Delta u_{solid} + v^0 \Delta P$$

$$\Delta h_{solid} = \Delta u_{solid} \cong C\Delta T$$

For **liquids**, two special cases are encountered:

1. **Constant-pressure processes**, as in heaters ( $\Delta P = 0$ )

$$\Delta h_{liquid} = \Delta u_{liquid} \cong C\Delta T$$

2. **Constant-temperature processes**, as in pumps ( $\Delta T = 0$ )

$$\Delta h_{liquid} = \Delta u_{liquid} + v\Delta P \cong C\Delta^0 T + v\Delta P$$

$$\Delta h_{liquid} = v\Delta P$$

We will derive this last expression for  $\Delta h$  again once we have discussed the first law for the open system in Chapter 4 and the second law of thermodynamics in Chapter 6.

The specific heats of selected liquids and solids are given in Table A-3.