

ESO201A : THERMODYNAMICS

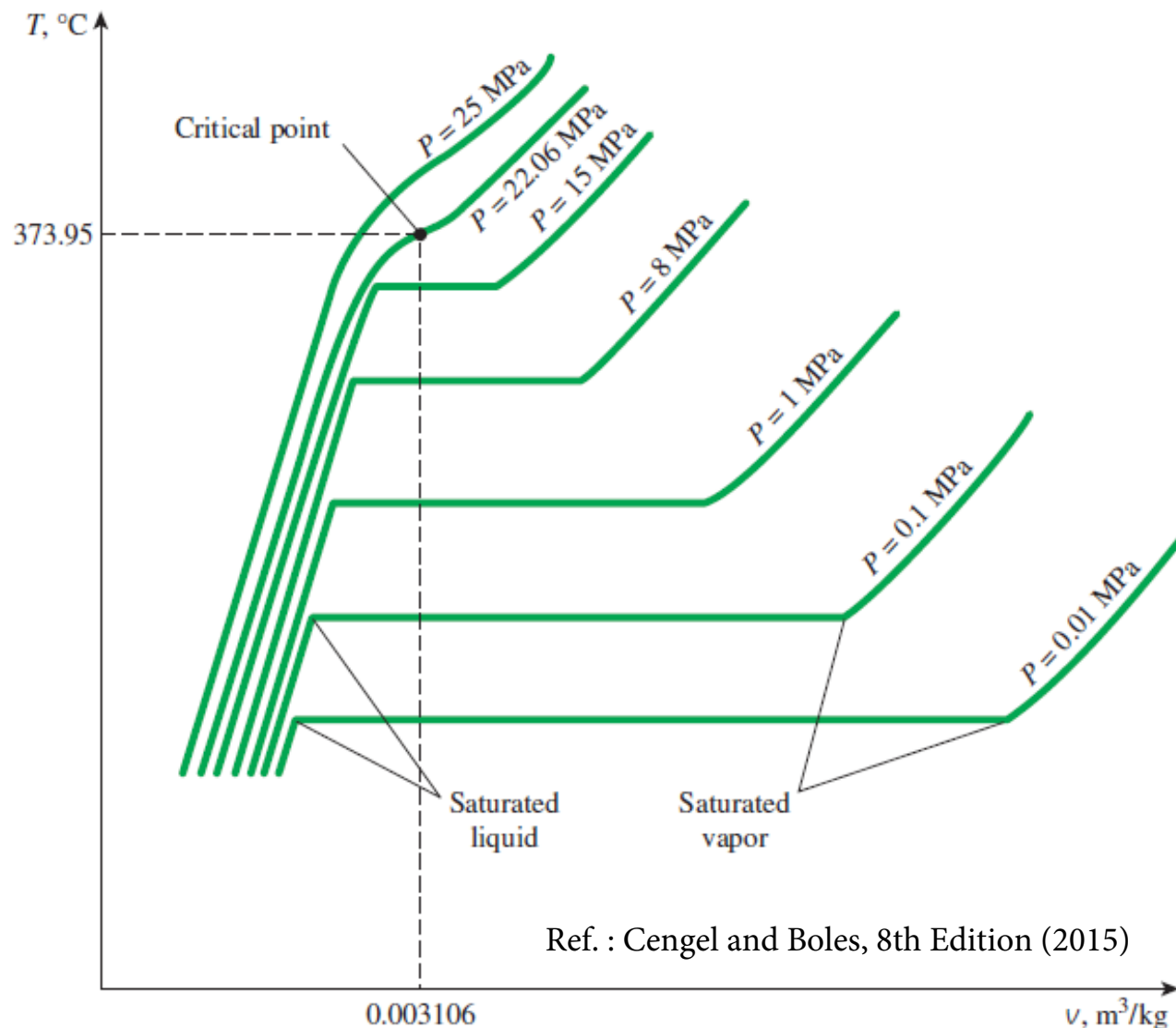
2021-22 1st semester

IIT Kanpur

Instructor : P.A.Apte

Lecture 5

Copyright: The instructor of this course (ESO201A) owns the copyright of all the course materials. The lecture material was distributed only to the students attending the course ESO201A of IIT Kanpur, and should not be distributed in print or through electronic media without the consent of the instructor. Students can make their own copies of the course materials for their use.

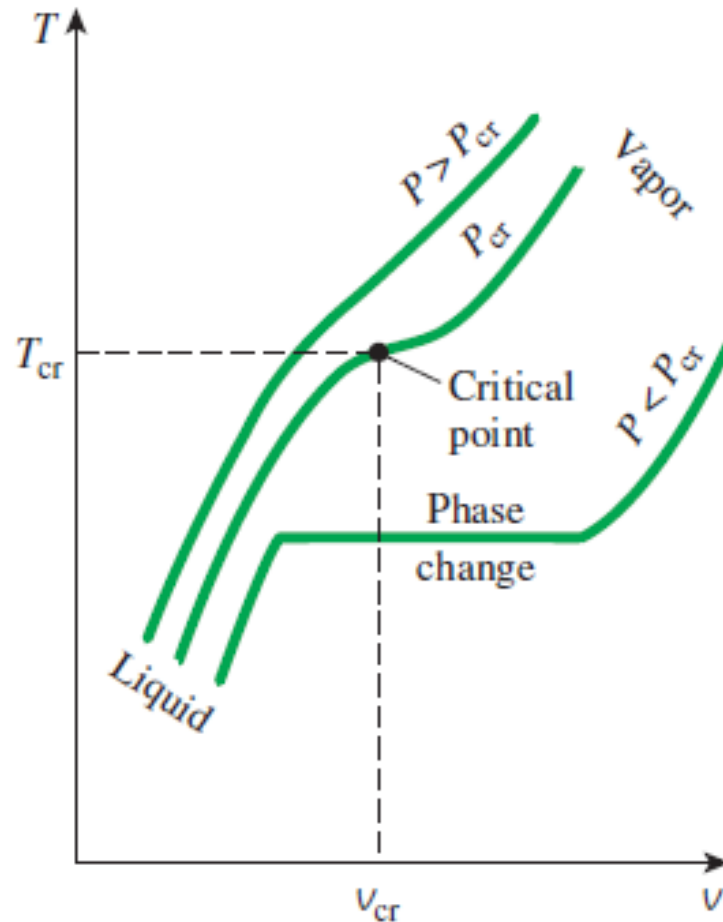


T-v plots resulting from constant pressure expansion of water at various pressures

NOTE : “critical” point occurs at $P_{\text{cr}} = 22.06 \text{ MPa}$, $T_{\text{cr}} = 373.95 ^\circ\text{C}$, $v_{\text{cr}} = 0.03106 \text{ m}^3/\text{kg}$

As critical point is approached, the saturated liquid and saturated vapor phases ‘merge’.

Constant pressure expansion :



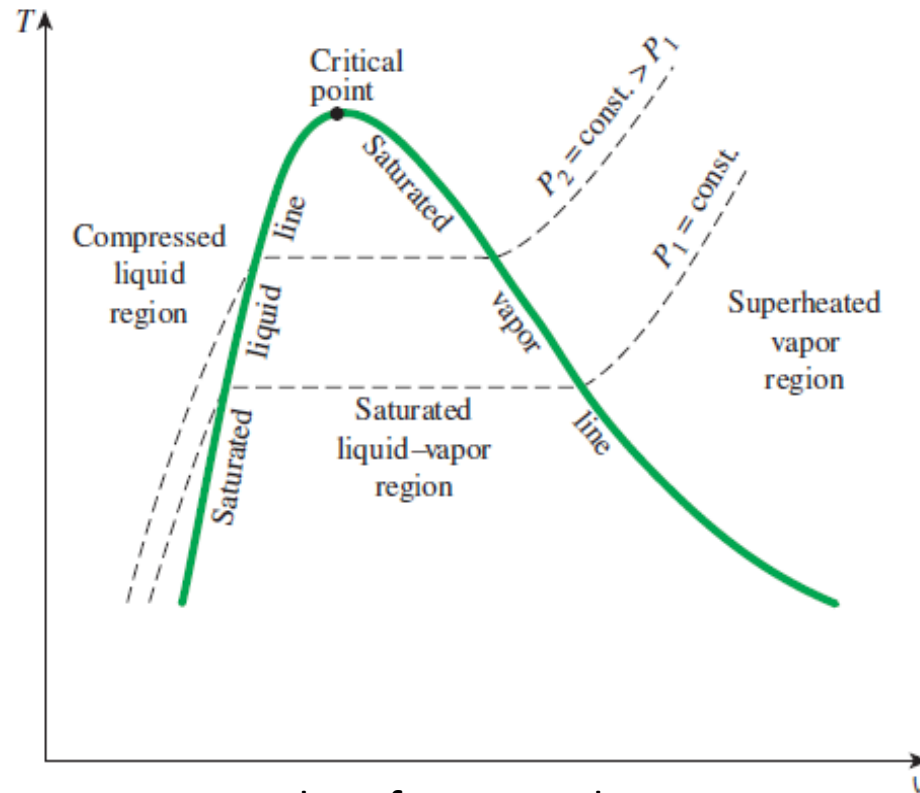
Note that above critical pressure ($P > P_{cr}$), no phase change is observed in constant pressure expansion

The state of the substance above critical pressure and critical temperature is called as “**gas**” since it does not condense upon cooling or compression

Property diagrams of a pure substance :

Note that $T_{\text{sat}} = f(P)$.

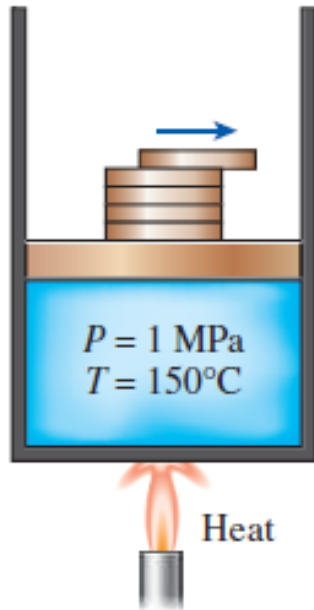
As P increases, T_{sat} also increases.



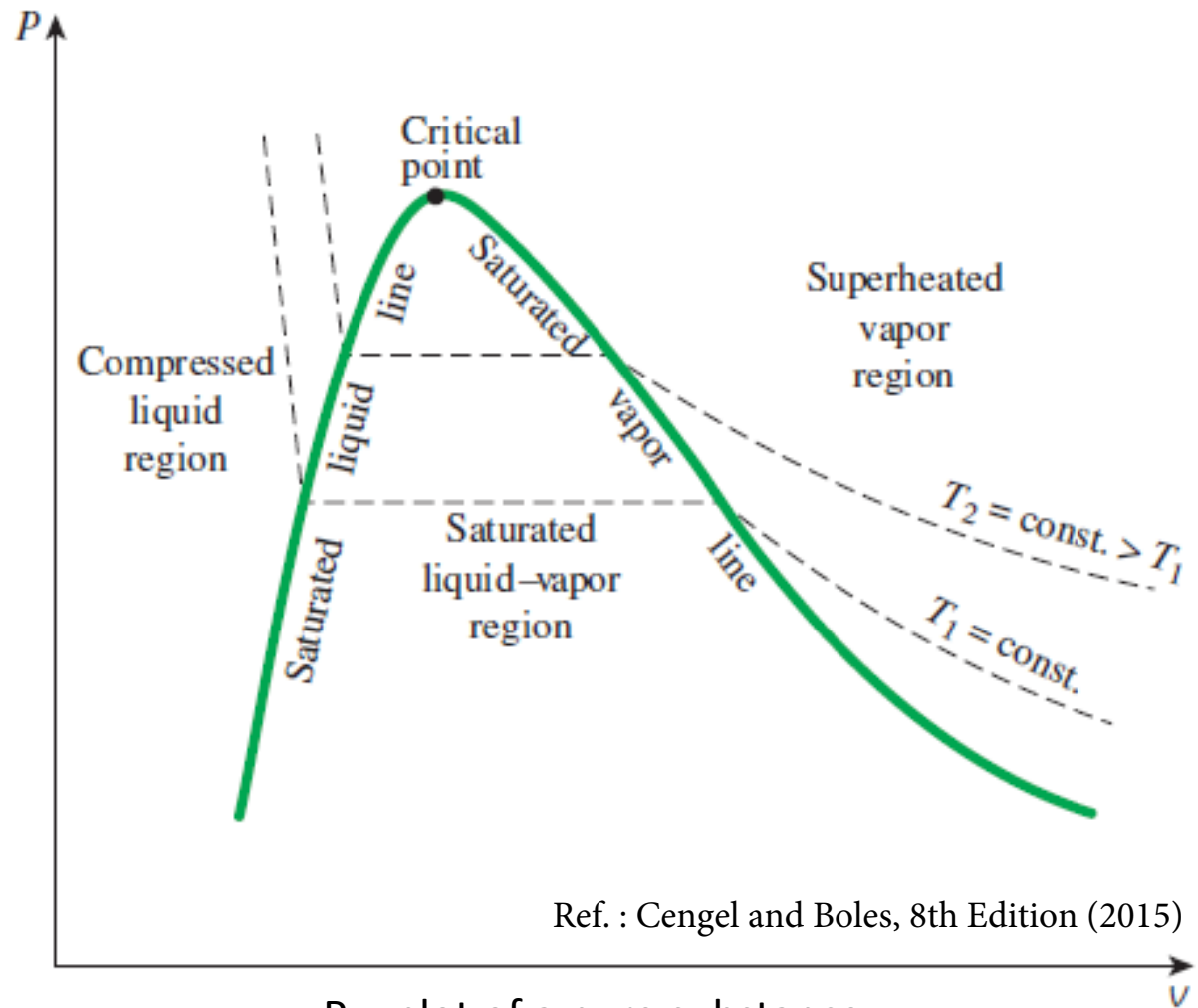
T-v plot of a pure substance

The green curve is known as “saturation curve”. It can be divided into two parts : one corresponding to saturated liquid and the other corresponding to saturated vapor. On the left hand side of the curve, below the critical point we have a region where liquid is the stable phase and is called as compressed liquid region. On the right hand side below the critical point, we have superheated vapor region. Here the vapor phase is the stable phase. Inside the curve we have two-phase region where both saturated liquid and saturated vapor coexist.

Constant temperature expansion of a pure substance :



The constant temperature expansion can be brought about by removing weights on the piston successively while providing heat so as to maintain constant temperature



P - v plot of a pure substance

At $P = P_{\text{sat}}$, expansion occurs at constant temperature and pressure.

Note also, that $P_{\text{sat}} = f(T)$. As T increases, P_{sat} also increases.

Phase changes involving solid phase:

There are two types of phase changes involving solid phase :
sublimation and melting

Melting involves solid to liquid transition at constant temperature and constant pressure.

Sublimation involves direct conversion of solid phase into vapor phase at constant temperature and constant pressure.

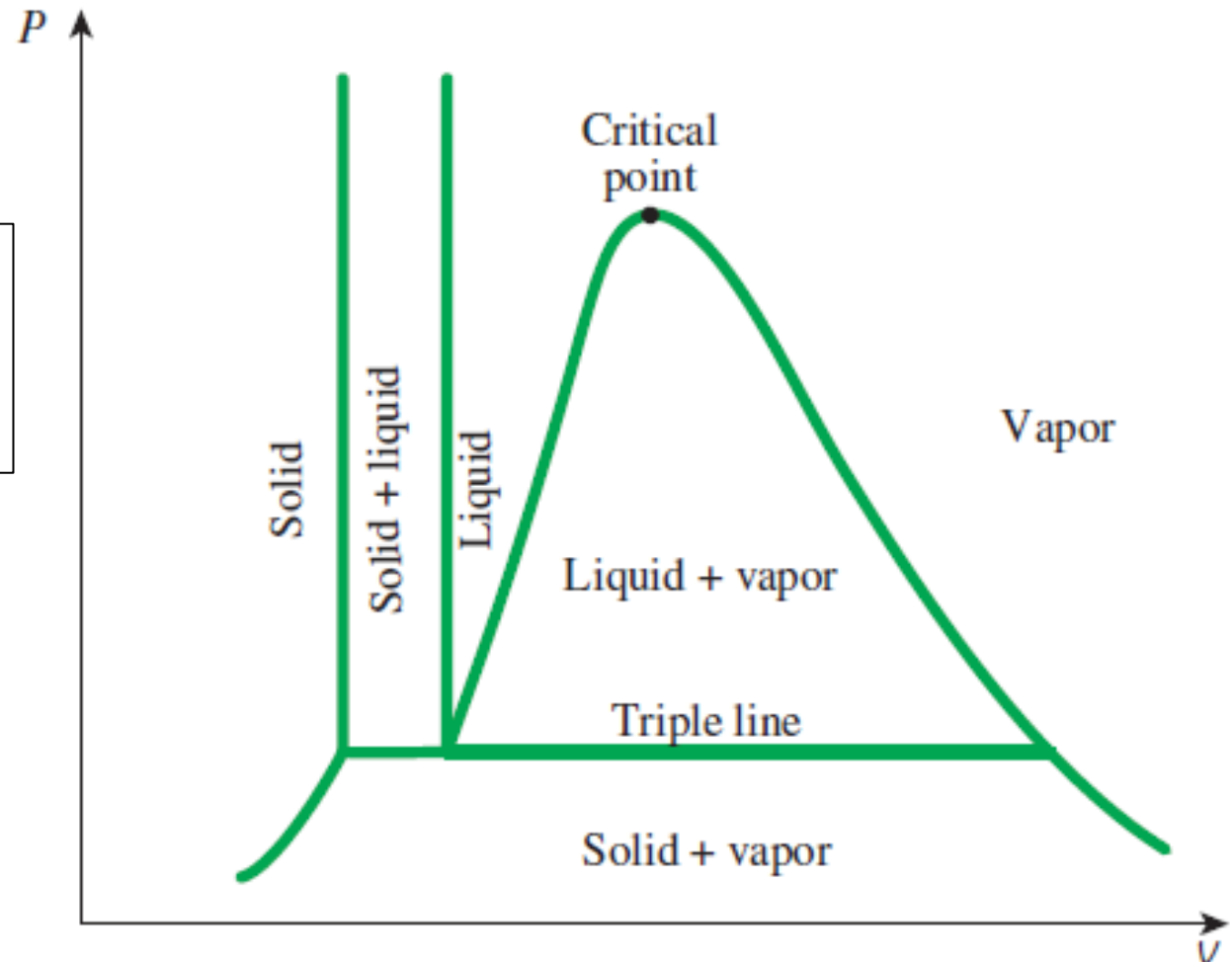
These changes can be brought about by constant pressure heating starting from the solid phase.

There are two phase regions (solid—vapor and solid—liquid) associated with sublimation and melting, just like in case of vaporization (liquid—vapor).

Constant temperature expansion of a pure substance :

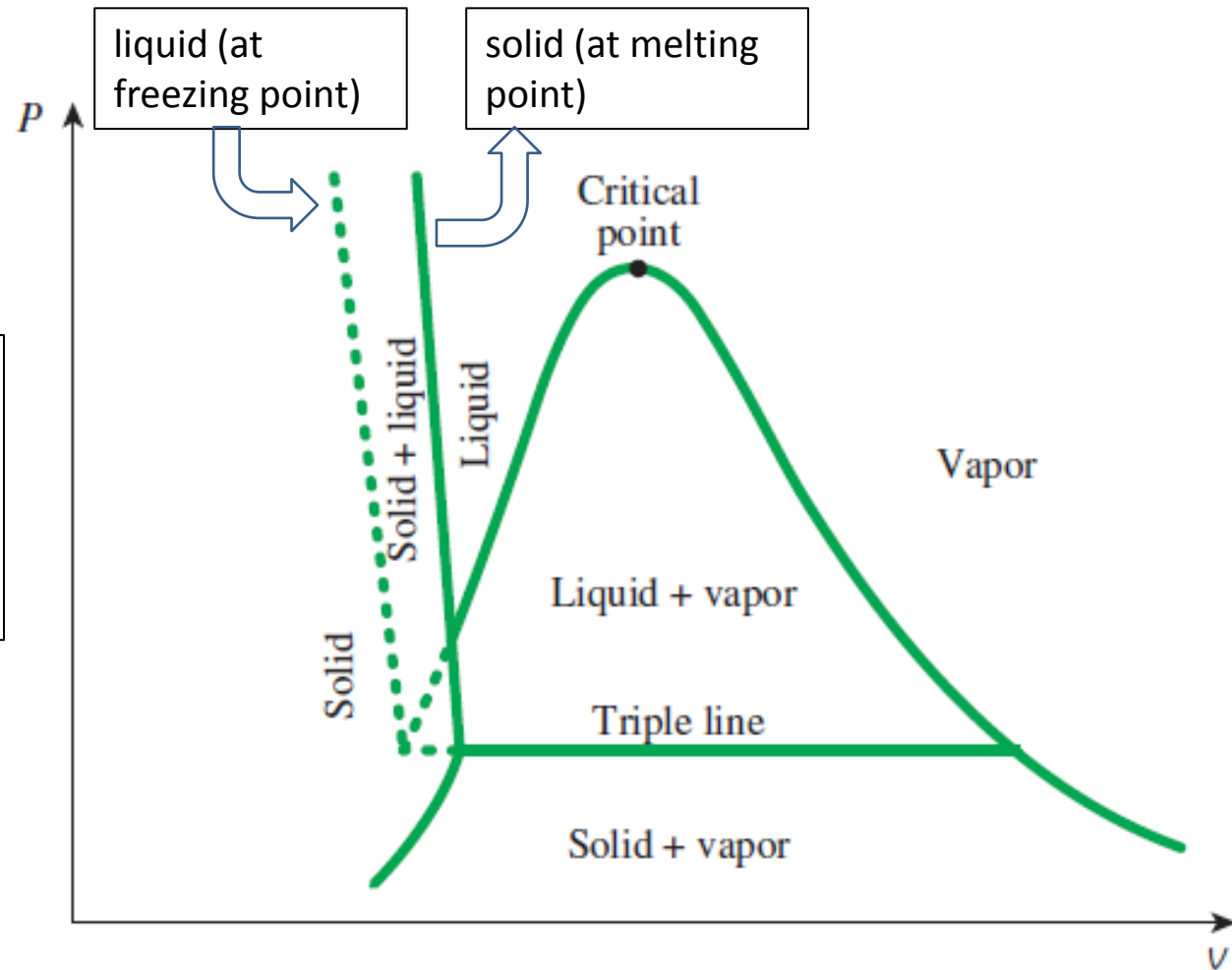
The P-v diagram resulting from constant temperature expansion of a pure substance involving all three phases is shown below:

This plot is for substances in which solid phase has a lower specific volume than the liquid phase at coexistence.



(a) P-v diagram of a substance that contracts on freezing

Constant temperature expansion of a pure substance :



(b) P - v diagram of a substance that expands on freezing (such as water)

Triple point of a pure substance :

Note that in the last two slides, triple line is seen which corresponds to the overall specific volume (v) of a system in which all three phases coexist.

Such a system exists at the temperature and pressure corresponding to a unique point known as “Triple point”

For water, triple point temperature and pressure are 0.01°C and 0.6117 kPa , respectively.

At a specific volume corresponding to the triple line (see last two slides), we have the condition :

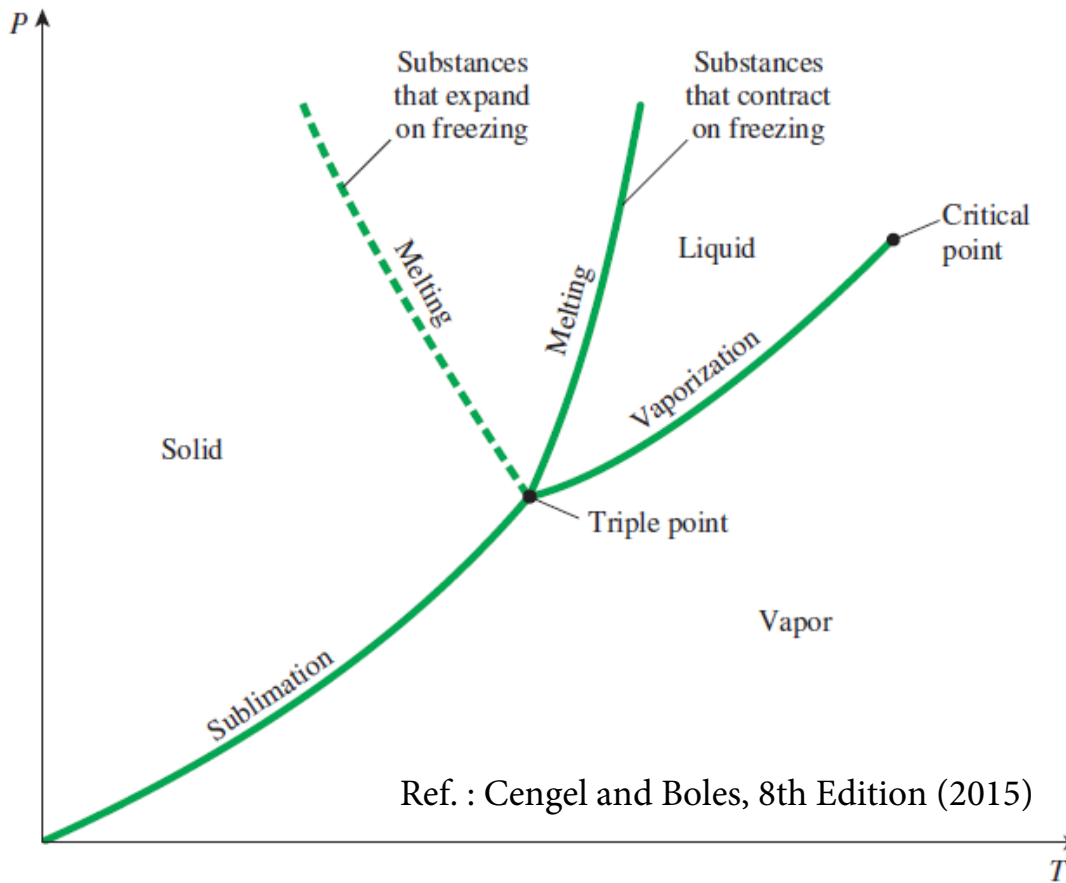
$$v = x_g v_g + x_f v_f + x_s v_s$$

$$x_g = \frac{m_g}{m_t}, \quad x_f = \frac{m_f}{m_t}, \quad x_s = \frac{m_s}{m_t}$$

m_g = mass of vapor phase, m_f = mass of liquid phase, m_s = mass of solid phase, and $m_t = (m_g + m_f + m_s)$ is the total mass



P-T diagram of a pure substance that exists in 3 phases:



- Unlike the P-v or T-v diagrams, there is no two phase region in P-T diagram.
- The green curves are also known as coexistence curves or saturation curves.
- Sublimation (solid-vapor transition) occurs below triple point temperature. For example, camphor undergoes sublimation at ambient conditions. This is because the triple point of camphor is at (180.1 °C; 51.44 kPa)

Property Tables : For water, these tables are as listed below (Table numbers refer to Appendix 1 of the textbook).

Saturated water – Temperature table (Table A-4)

Saturated water – Pressure table (Table A-5)

Superheated water (Table A-6)

Compressed liquid water (Table A-7)

Table A-4 is partially reproduced below. Note that subscript “f” and “g” refer to saturated liquid and saturated vapor at the given temperature. “u” is internal energy per unit mass and “s” is a property known as entropy (which we will explain later in the course) per unit mass. P_{sat} is the saturation pressure at the given temperature.

Ref. : Cengel and Boles, 8th Edition (2015)

TABLE A-4

Saturated water—Temperature table

Temp., T °C	Sat. press., P_{sat} kPa	Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg·K		
		Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
0.01	0.6117	0.001000	206.00	0.000	2374.9	2374.9	0.001	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.019	2360.8	2381.8	21.020	2489.1	2510.1	0.0763	8.9487	9.0249
10	1.2281	0.001000	106.32	42.020	2346.6	2388.7	42.022	2477.2	2519.2	0.1511	8.7488	8.8999
15	1.7057	0.001001	77.885	62.980	2332.5	2395.5	62.982	2465.4	2528.3	0.2245	8.5559	8.7803
20	2.3392	0.001002	57.762	83.913	2318.4	2402.3	83.915	2453.5	2537.4	0.2965	8.3696	8.6661

Reference states for the property tables:

Ref. : Cengel and Boles, 8th Edition (2015)

The absolute values of properties like internal energy cannot be measured. However as demonstrated by Joule's experiments, change in internal energy can be measured. Hence a convenient reference state is chosen at which properties such as internal energy and entropy are taken as zero.

For water, the reference state is liquid water at the triple point. The first row of the Tables A-4 (previous slide) corresponds to the triple point. In the first row (triple point) of Table A-4 , $u_f = 0$, $s_f = 0$.

Saturated water—Pressure table (A-5) is reproduced below partially.

TABLE A-5

Saturated water—Pressure table

Press., P kPa	Sat. temp., T_{sat} °C	Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, $\text{kJ/kg}\cdot\text{K}$		
		Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
1.0	6.97	0.001000	129.19	29.302	2355.2	2384.5	29.303	2484.4	2513.7	0.1059	8.8690	8.9749
1.5	13.02	0.001001	87.964	54.686	2338.1	2392.8	54.688	2470.1	2524.7	0.1956	8.6314	8.8270
2.0	17.50	0.001001	66.990	73.431	2325.5	2398.9	73.433	2459.5	2532.9	0.2606	8.4621	8.7227
2.5	21.08	0.001002	54.242	88.422	2315.4	2403.8	88.424	2451.0	2539.4	0.3118	8.3302	8.6421
3.0	24.08	0.001003	45.654	100.98	2306.9	2407.9	100.98	2443.9	2544.8	0.3543	8.2222	8.5765

Property tables:

Note that in Tables A-4 and A-5, the symbol “fg” refers to the difference between properties of saturated liquid (f) and saturated vapor (g).

For example, $h_{fg} = h_g - h_f$. This quantity (h_{fg}) is known as **enthalpy of vaporization** (or latent heat of vaporization).

The values of v_{fg} , u_{fg} , h_{fg} , and s_{fg} decreases with increasing temperature or increasing pressure and becomes **zero** at the critical point. This is because the saturated liquid and saturated vapor states approach each other as we approach critical point upon increasing pressure or increasing temperature (see previous slides).

Example : A mass of 1 kg of saturated liquid water is completely vaporized to saturated vapor at constant pressure of 100 kPa. Determine (a) volume change (b) the heat transferred to water assuming slow expansion

Solution : Since it's a constant pressure process involving saturated liquid and saturated vapor, we will use Table A-5. The relevant portion of Table A-5 is reproduced below.

$$\begin{aligned}\text{Volume change is : } \Delta V &= m(v_g - v_f) \\ &= (1)(1.6941 - 0.001043) \\ &= 1.693 \text{ m}^3\end{aligned}$$

Heat transferred (assuming slow expansion) is :

$$\begin{aligned}Q_{in} &= m(h_g - h_f) \text{ [Since it's a constant pressure process]} \\ &= (1)(2257.5) \\ &= 2257.5 \text{ kJ}\end{aligned}$$

Ref. : Cengel and Boles, 8th Edition (2015)

Saturated water—Pressure table

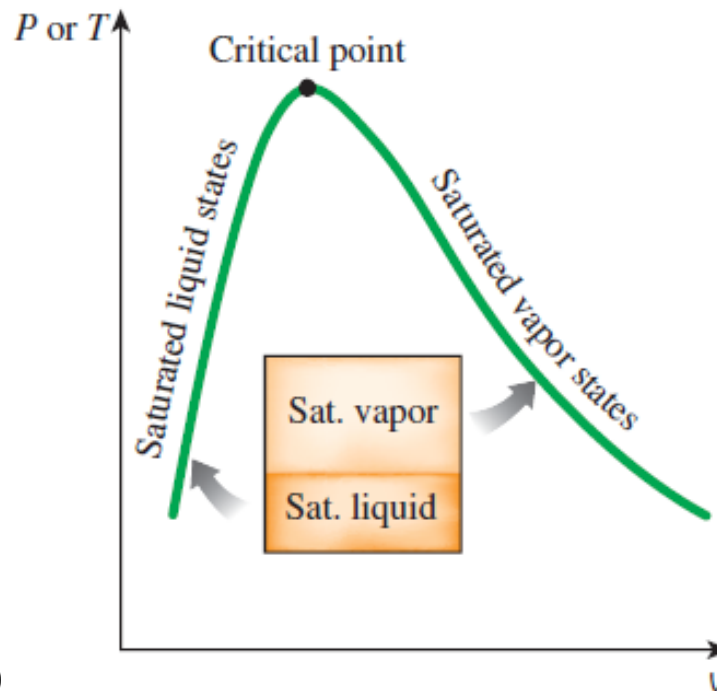
Press., <i>P</i> kPa	Sat. temp., <i>T</i> _{sat} °C	Specific volume, m ³ /kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg·K		
		Sat. liquid, <i>v</i> _f	Sat. vapor, <i>v</i> _g	Sat. liquid, <i>u</i> _f	Evap., <i>u</i> _{fg}	Sat. vapor, <i>u</i> _g	Sat. liquid, <i>h</i> _f	Evap., <i>h</i> _{fg}	Sat. vapor, <i>h</i> _g	Sat. liquid, <i>s</i> _f	Evap., <i>s</i> _{fg}	Sat. vapor, <i>s</i> _g
100	99.61	0.001043	1.6941	417.40	2088.2	2505.6	417.51	2257.5	2675.0	1.3028	6.0562	7.3589

Mixture of saturated liquid and saturated vapor:

In certain processes, we deal with a mixture in which saturated liquid and saturated vapor are present. The specific volume of such a mixture corresponds to the area inside the saturation curve shown below.

The specific volume of this mixture is obtained as follows : $v = (1-x) v_f + x v_g$

where $x = m_g/m_t$ is the mass fraction of the vapor phase and $m_t = (m_f + m_g)$ is the total mass. The quantity 'x' is often referred to as the **dryness fraction** or the **quality**. Similarly we can calculate other specific properties of the mixture.



Superheated water table:

Superheated water table (A-6) is reproduced below partially. Note that in this table (A-6), the temperature in the parenthesis corresponds to the saturation temperature at given pressure. For example, at $P = 0.01 \text{ MPa}$, $T_{\text{sat}} = 45.81^\circ\text{C}$. The properties of saturated vapor at $P = 0.01 \text{ MPa}$ are listed in the top row starting with the letters “Sat.”

TABLE A-6

Superheated water

T $^\circ\text{C}$	v m^3/kg	u kJ/kg	h kJ/kg	s $\text{kJ/kg}\cdot\text{K}$	v m^3/kg	u kJ/kg	h kJ/kg	s $\text{kJ/kg}\cdot\text{K}$	v m^3/kg	u kJ/kg	h kJ/kg	s $\text{kJ/kg}\cdot\text{K}$
	$P = 0.01 \text{ MPa } (45.81^\circ\text{C})^*$				$P = 0.05 \text{ MPa } (81.32^\circ\text{C})$				$P = 0.10 \text{ MPa } (99.61^\circ\text{C})$			
Sat. [†]	14.670	2437.2	2583.9	8.1488	3.2403	2483.2	2645.2	7.5931	1.6941	2505.6	2675.0	7.3589
50	14.867	2443.3	2592.0	8.1741								
100	17.196	2515.5	2687.5	8.4489	3.4187	2511.5	2682.4	7.6953	1.6959	2506.2	2675.8	7.3611
150	19.513	2587.9	2783.0	8.6893	3.8897	2585.7	2780.2	7.9413	1.9367	2582.9	2776.6	7.6148
200	21.826	2661.4	2879.6	8.9049	4.3562	2660.0	2877.8	8.1592	2.1724	2658.2	2875.5	7.8356
250	24.136	2736.1	2977.5	9.1015	4.8206	2735.1	2976.2	8.3568	2.4062	2733.9	2974.5	8.0346
300	26.446	2812.3	3076.7	9.2827	5.2841	2811.6	3075.8	8.5387	2.6389	2810.7	3074.5	8.2172

Properties of compressed liquid:

As per the state postulate, the state of compressed liquid is completely determined by specifying temperature (T) and pressure (P). For a compressed liquid, $P > P_{\text{sat}}$ where P_{sat} is the saturation pressure at T . The properties of compressed liquid (Table A-7) are listed only for a limited set of conditions. Since liquid properties are not strongly affected by pressure, the following approximation can be made to estimate compressed liquid properties in case these are not explicitly available in tables:

$$u(T,P) \approx u_{f@T}, \quad v(T,P) \approx v_{f@T}, \quad s(T,P) \approx s_{f@T}$$

Please note that

$$u_{f@T} = u(T, P_{\text{sat}})$$

$$v_{f@T} = v(T, P_{\text{sat}})$$

$$s_{f@T} = s(T, P_{\text{sat}})$$

Properties of compressed liquid:

The specific enthalpy of a compressed liquid is estimated as :

$$\begin{aligned} h(T,P) - h(T,P_{\text{sat}}) &= \int_{P_{\text{sat}}}^P \left(\frac{\partial h}{\partial P} \right)_T dP \\ &= \int_{P_{\text{sat}}}^P \left(\frac{\partial(u + Pv)}{\partial P} \right)_T dP \\ &\approx v_{f@P_{\text{sat}}} (P - P_{\text{sat}}) \end{aligned}$$

In the above derivation, pressure dependence of u and v at constant T has been neglected. Also, the remaining integral term has been simplified using the approximation

$$v(T, P) \approx v(T, P_{\text{sat}}) = v_{f@T} \text{ (independent of } P\text{)}.$$

Since $h(T, P_{\text{sat}}) = h_{f@T}$, the above equation can be re-arranged as:

$$\boxed{h(T,P) \approx h_{f@T} + v_{f@T} (P - P_{\text{sat}})}$$

Example: Determine the enthalpy of compressed liquid water at 80 °C and 5 MPa using (a) compressed liquid data and (b) saturated liquid data. What is the error involved in the second case.

Solution : Relevant part of the compressed liquid table (A-7) is reproduced below. (a) Using Table A-7, the internal energy is $h = 338.96$ kJ/kg

Ref. : Cengel and Boles, 8th Edition (2015)

TABLE A-7

Compressed liquid water

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K
$P = 5$ MPa (263.94°C)					$P = 10$ MPa (311.00°C)				$P = 15$ MPa (342.16°C)			
80	0.0010267	333.82	338.96	1.0723	0.0010244	332.69	342.94	1.0691	0.0010221	331.59	346.92	1.0659

(b) Using saturated liquid data (Table A-4) see below, and expression on last slide

$$h \approx h_{f@80^\circ\text{C}} + v_{f@80^\circ\text{C}}(P - P_{\text{sat}}) = 335.02 + (0.001029)(5000 - 47.416) = 340.11 \text{ kJ/kg.}$$

The percentage of error involved is $= (340.11 - 338.96)(100)/(338.96) = 0.34 \%$

This error is small and hence the approximation used in (b) is good.

TABLE A-4

Saturated water—Temperature table

Temp., T °C	Sat. press., P_{sat} kPa	Specific volume, m ³ /kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg·K		
		Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
80	47.416	0.001029	3.4053	334.97	2146.6	2481.6	335.02	2308.0	2643.0	1.0756	6.5355	7.6111