

Analysis of processes involving **pure** substance:

If a substance (which has a fixed chemical composition throughout) does not undergo a change in composition, it can be considered as a pure substance

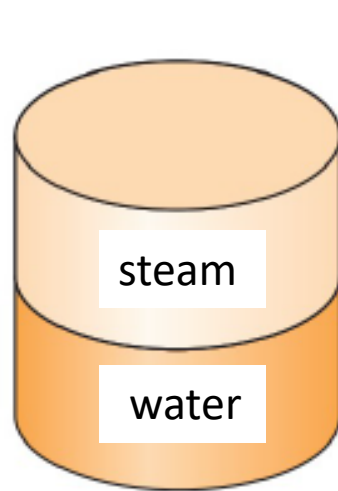
A pure substance need not contain a single element or a single compound.



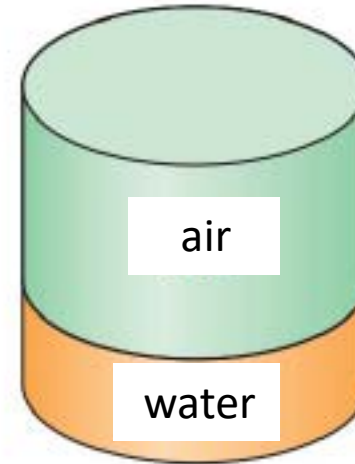
Air contains N_2 , O_2 , and small amounts of other gases

In processes NOT involving change of composition, air is treated as a pure substance

Analysis of processes involving **pure** substance:

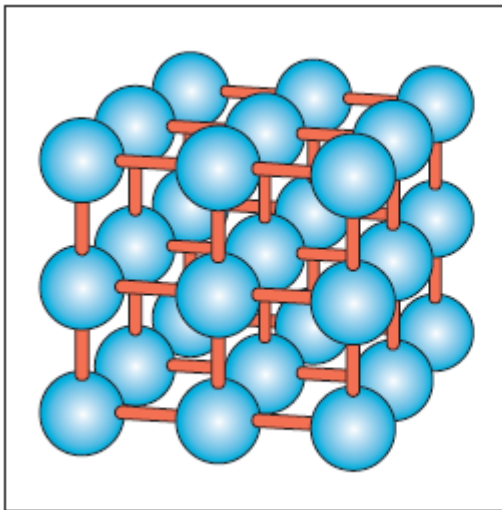


(water + steam) is a pure substance

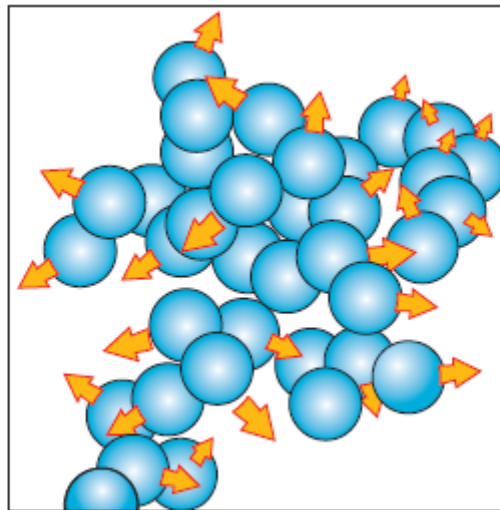


(water + air) is NOT a pure substance

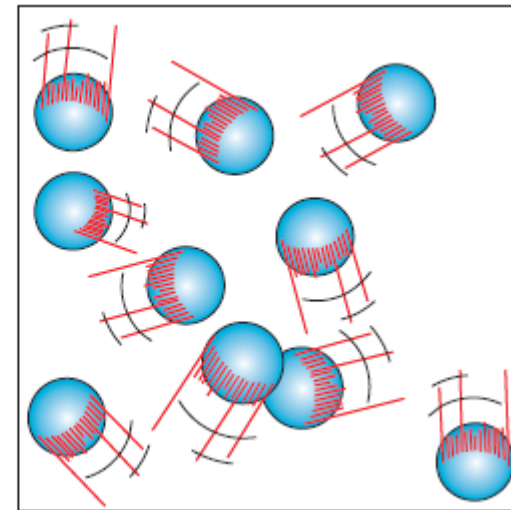
A pure substance can exist in different phases



SOLID



LIQUID



GAS

Gaseous state :

A pure substance is said to be in a gaseous state if it does not condense upon cooling or compression in a given process.

Thus if the temperature and pressure of a pure substance is above the values corresponding to critical point, then it is generally considered as a “gas”.

Recall that according to the **state postulate** (based on experimental observations) , the state of a single phase of a pure substance is completely determined by specifying two independent, intensive variables.

The state postulate certainly applies to a gas.

Equation of state :

Thus state postulate implies that if we consider any intensive property θ , then $\theta = f(T,P)$ or $\theta = g(T,v)$. This is because (T,P) and (T,v) are sets of two independent intensive variables. The property θ can be specific heat, specific volume, viscosity etc.

If we use $\theta = v$ (specific volume), then $v = f(T,P)$. This equation is known as “Equation of state”. Note that v , T , P are all experimentally measurable properties. Hence equation of state can be obtained from experimental measurements.

If we make certain approximations, we can obtain equation of state theoretically (using statistical mechanics). One such approximation is to assume that a given gas phase is an “Ideal gas”, i.e., the constituent molecules/atoms of the gas do not interact with each other.

Ideal gas equation of state :

For an ideal gas, it can be shown that

$$v = \frac{RT}{P}, \text{ where } R = \frac{R_u}{M}$$

$R_u = 8.314 \text{ kJ}/(\text{kmol}\cdot\text{K})$ is universal gas constant, and

M = molecular weight in (kg/kmol) or (g/mol)

For example, for N_2 , $M = 28 \text{ kg/kmol}$ and hence $R = 0.297 \text{ kJ}/(\text{kg}\cdot\text{K})$

Table A-1 (of textbook) lists M , R , and critical points for several gases.

It is partially reproduced below :

TABLE A-1						
Molar mass, gas constant, and critical-point properties						
Substance	Formula	Molar mass, M kg/kmol	Gas constant, R kJ/kg·K*	Critical-point properties		
				Temperature, K	Pressure, MPa	Volume, m^3/kmol
Air	—	28.97	0.2870	132.5	3.77	0.0883
Ammonia	NH_3	17.03	0.4882	405.5	11.28	0.0724
Argon	Ar	39.948	0.2081	151	4.86	0.0749
Benzene	C_6H_6	78.115	0.1064	562	4.92	0.2603
Bromine	Br_2	159.808	0.0520	584	10.34	0.1355
<i>n</i> -Butane	C_4H_{10}	58.124	0.1430	425.2	3.80	0.2547
Carbon dioxide	CO_2	44.01	0.1889	304.2	7.39	0.0943
Carbon monoxide	CO	28.011	0.2968	133	3.50	0.0930
Carbon tetrachloride	CCl_4	153.82	0.05405	556.4	4.56	0.2759
Chlorine	Cl_2	70.906	0.1173	417	7.71	0.1242
Chloroform	CHCl_3	119.38	0.06964	536.6	5.47	0.2403
Dichlorodifluoromethane (R-12)	CCl_2F_2	120.91	0.06876	384.7	4.01	0.2179
Dichlorofluoromethane (R-21)	CHCl_2F	102.92	0.08078	451.7	5.17	0.1973
Ethane	C_2H_6	30.070	0.2765	305.5	4.48	0.1480

When can a gas be approximated as an ideal gas ?

In general, when the constituent molecules/atoms are far apart from each other, there is not a significant intermolecular interaction

This condition is approached as we increase the temperature or decrease the pressure of the gas. Generally under ambient conditions ($P = 1 \text{ atm}$ and $T = 25^\circ\text{C}$), many gases can be considered as ideal gases to a good degree of approximation.

Can water vapor be considered as Ideal gas ?

Generally if the pressure of water vapor is less than 10 kPa, then yes ! It can be considered as ideal gas without introducing serious error in calculations.

Properties of water vapor can be accurately obtained through 'steam tables'. (more on this in later slides)

Compressibility factor (Z):

It measures the deviation of the actual gas from ideal-gas behavior.

It is defined as follows: $Z = \frac{Pv}{RT}$

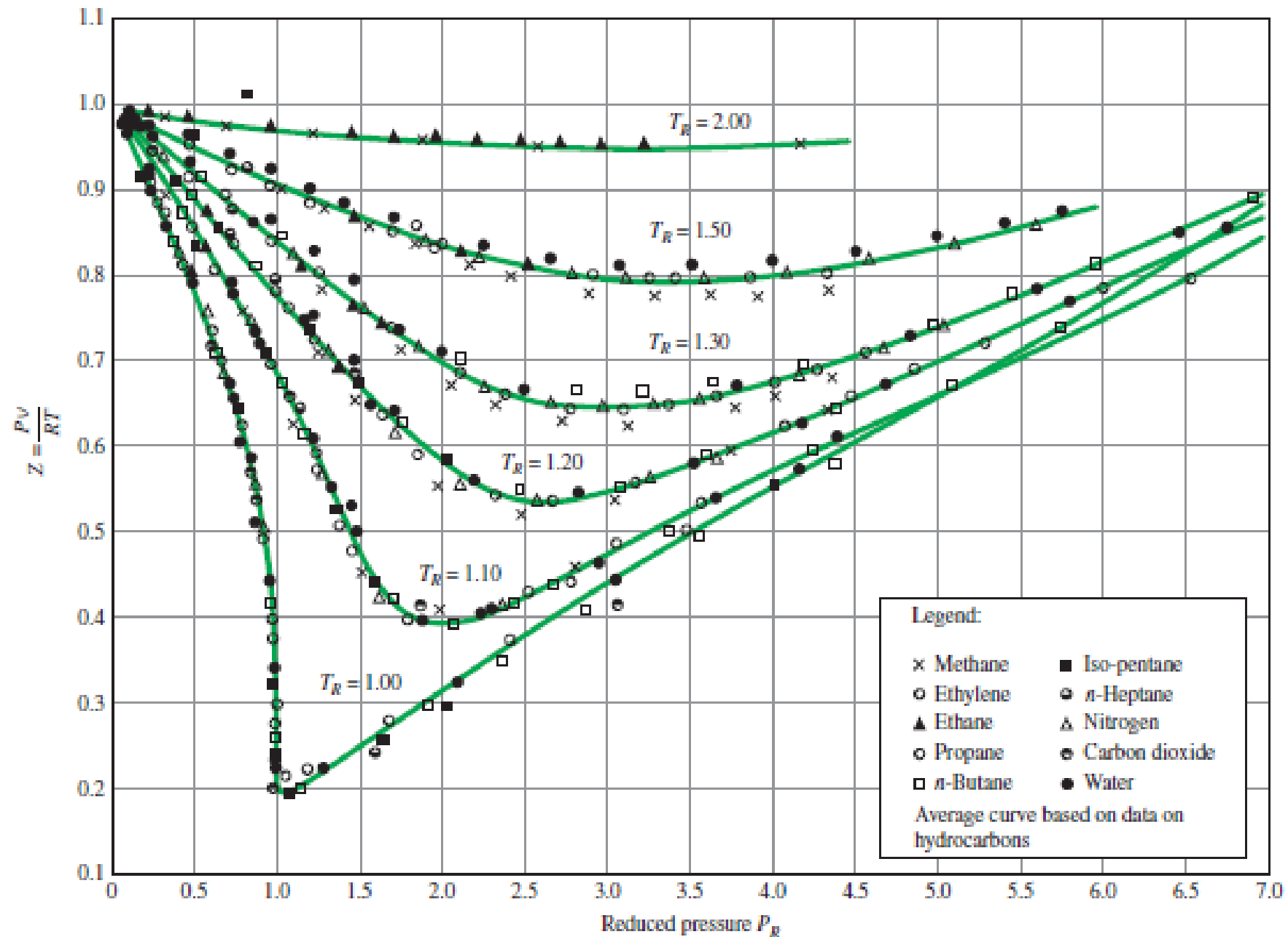
Note that for an ideal gas, $Z = 1$. It has been experimentally observed that :

The values of Z at a given reduced temperature (T_R) and reduced pressure (P_R) are approximately the same for all gases.

This is known as principle of corresponding states. although the word “principle” is used, it is just an approximation. Here, T_R and P_R are defined as

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

Comparison of Z factors for several gases:



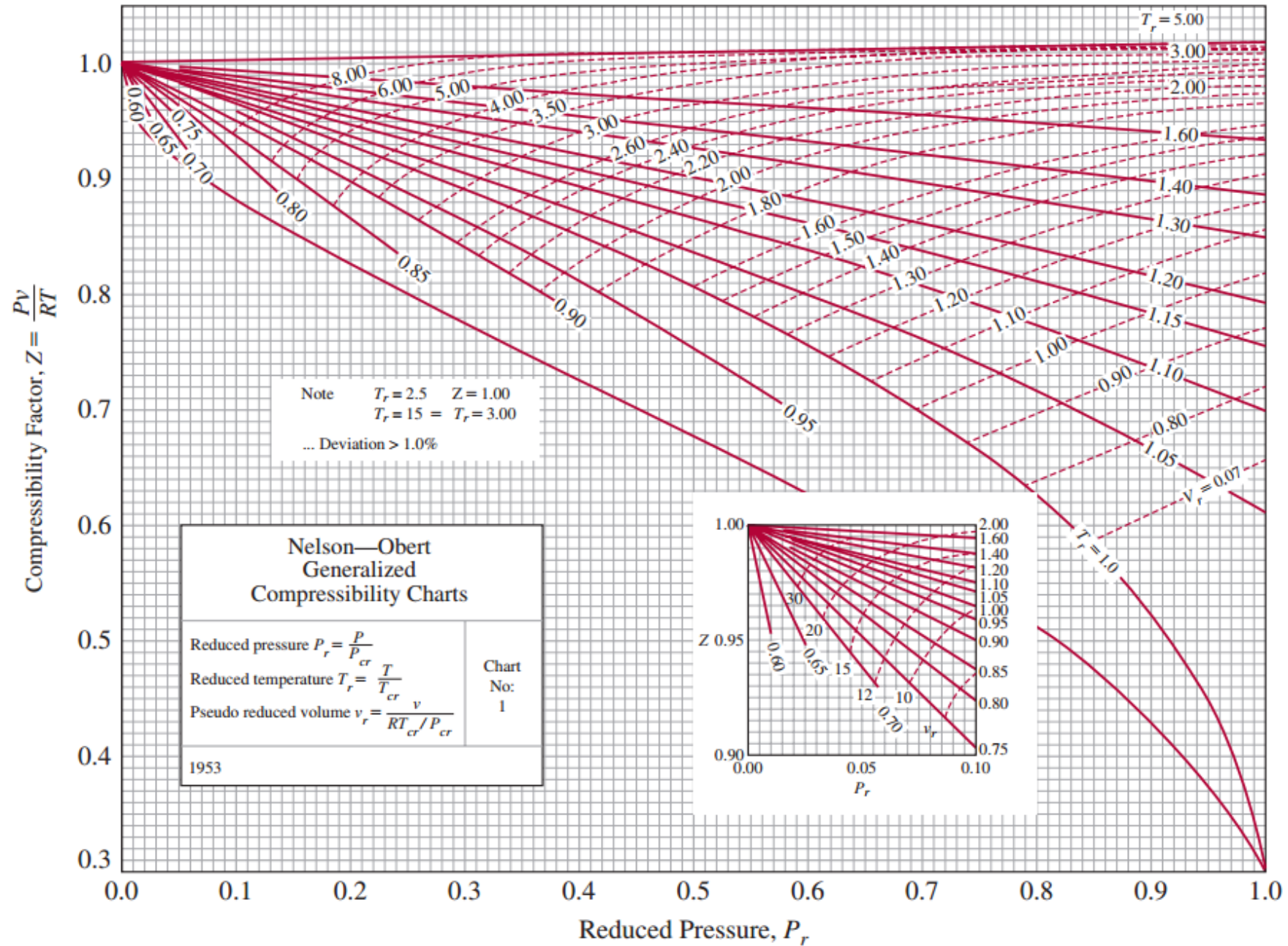
Comparison of Z factors for several gases:

Based on the experimental values of Z plotted on previous slide, it can be observed that :

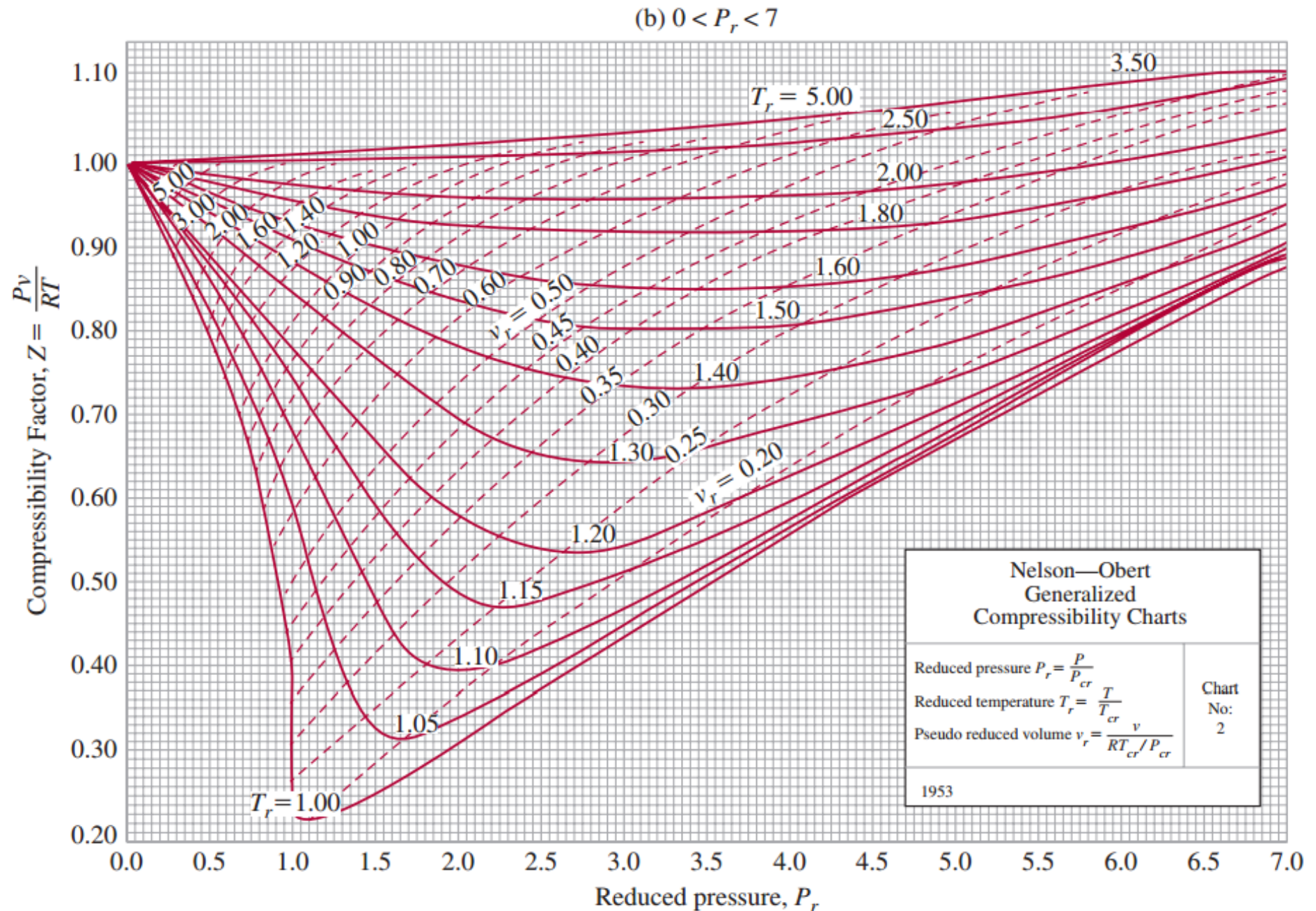
- (1) At very low pressures ($P_R \ll 1$) gas behaves as ideal gas irrespective of temperature
- (2) At $T_R > 2$, ideal gas behavior can be assumed with good accuracy except when $P_R \gg 1$
- (3) The deviation from ideal gas behavior is the greatest in the vicinity of critical point ($T_R = 1$, $P_R = 1$)

Generalized compressibility chart :

(a) $0 < P_r < 1.0$



Generalized compressibility chart :



Example :

Determine the specific volume of refrigerant-134a at 1 MPa and 50°C, using (a) the ideal-gas equation of state and (b) the generalized compressibility chart. Compare the values obtained to the actual value of 0.021796 m³/kg and determine the error involved in each case.

SOLUTION The specific volume of refrigerant-134a is to be determined assuming ideal- and nonideal-gas behavior.

Analysis The gas constant, the critical pressure, and the critical temperature of refrigerant-134a are determined from Table A–1 to be

$$R = 0.0815 \text{ kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K}$$

$$P_{\text{cr}} = 4.059 \text{ MPa}$$

$$T_{\text{cr}} = 374.2 \text{ K}$$

(a) The specific volume of refrigerant-134a under the ideal-gas assumption is

$$\nu = \frac{RT}{P} = \frac{(0.0815 \text{ kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})(323 \text{ K})}{1000 \text{ kPa}} = \mathbf{0.026325 \text{ m}^3/\text{kg}}$$

Therefore, treating the refrigerant-134a vapor as an ideal gas would result in an error of $(0.026325 - 0.021796)/0.021796 = 0.208$, or 20.8 percent in this case.

Example :

(b) To determine the correction factor Z from the compressibility chart, we first need to calculate the reduced pressure and temperature:

$$\left. \begin{aligned} P_R &= \frac{P}{P_{cr}} = \frac{1 \text{ MPa}}{4.059 \text{ MPa}} = 0.246 \\ T_R &= \frac{T}{T_{cr}} = \frac{323 \text{ K}}{374.2 \text{ K}} = 0.863 \end{aligned} \right\} Z = 0.84$$

Thus

$$\nu = Z\nu_{ideal} = (0.84)(0.026325 \text{ m}^3/\text{kg}) = \mathbf{0.022113 \text{ m}^3/\text{kg}}$$

Discussion The error in this result is less than **2 percent**. Therefore, in the absence of tabulated data, the generalized compressibility chart can be used with confidence.

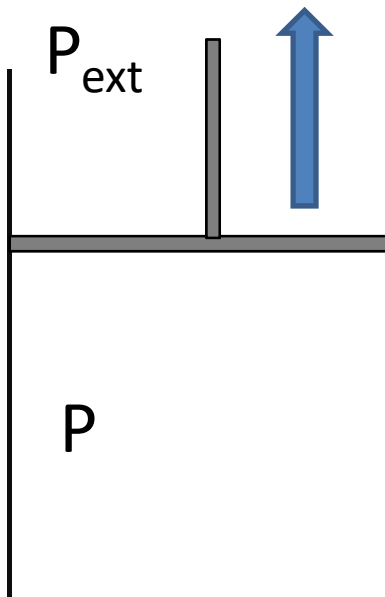
Note that the Z value reported above can be read from the generalized compressibility chart.

Expansion of a pure substance :

In an expansion process of a pure substance NOT involving changes in kinetic or potential energies, first law of thermodynamics states that :

$$U_2 - U_1 = Q_{\text{in}} - W_{\text{out}}$$

where, $W_{\text{out}} = \int_1^2 P_{\text{ext}} dV$



For an expansion process, $P > P_{\text{ext}}$

Therefore, one can write

$$(P - \Delta P) = P_{\text{ext}}$$

Expansion of a pure substance :

$$Q_{in} = (U_2 - U_1) + \int_1^2 P dV - \int_1^2 (\Delta P) dV$$

For a sufficiently slow expansion process, $\Delta P \rightarrow 0$. Hence third term on the right hand side of above equation can be neglected in comparison with the second term. So, for a slow expansion,

$$Q_{in} = (U_2 - U_1) + \int_1^2 P dV$$

If the expansion is sufficiently slow so that pressure is constant throughout the process, the above equation reduces to

$$Q_{in} = (U_2 - U_1) + P(V_2 - V_1)$$

$$Q_{in} = H_2 - H_1$$

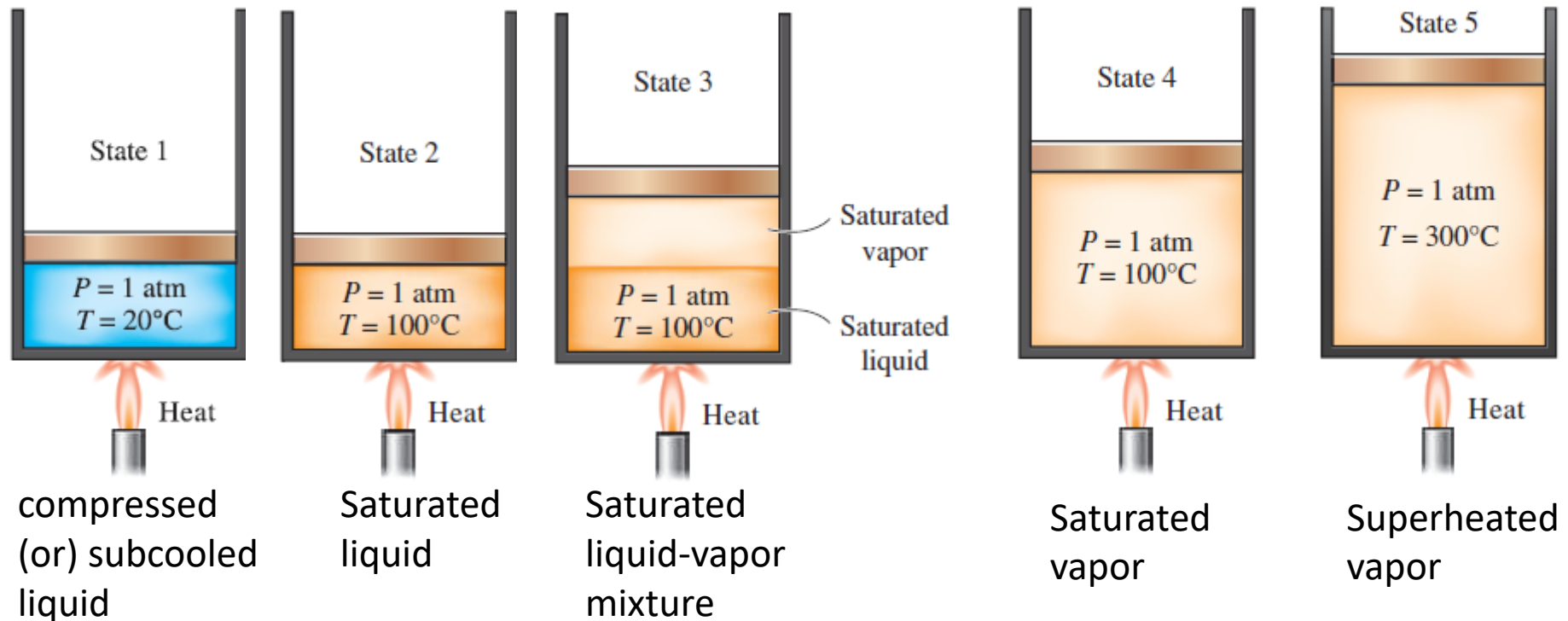


Here, $H = (U + PV)$ is the **Enthalpy**. **Enthalpy** is a state property

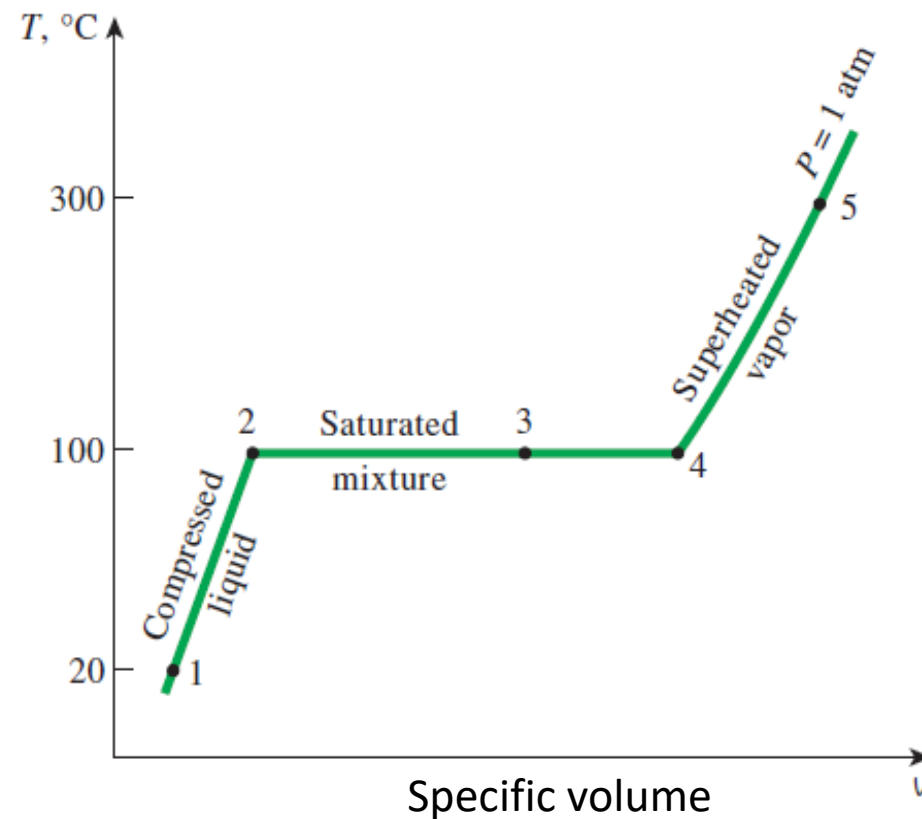
Constant pressure expansion of water :

The previous derivation shows that the heat absorbed by system in a sufficiently slow expansion at constant pressure is equal to increase of enthalpy of the substance.

Constant pressure expansion of water to steam at $P = 1 \text{ atm}$ (101.325 N/m^2)



Constant pressure expansion of water at 1 atm :



Note that based on Joule's experiments, these changes of state of water from 1 to 5 can also be brought about by performing mechanical work by enclosing water in adiabatic container.

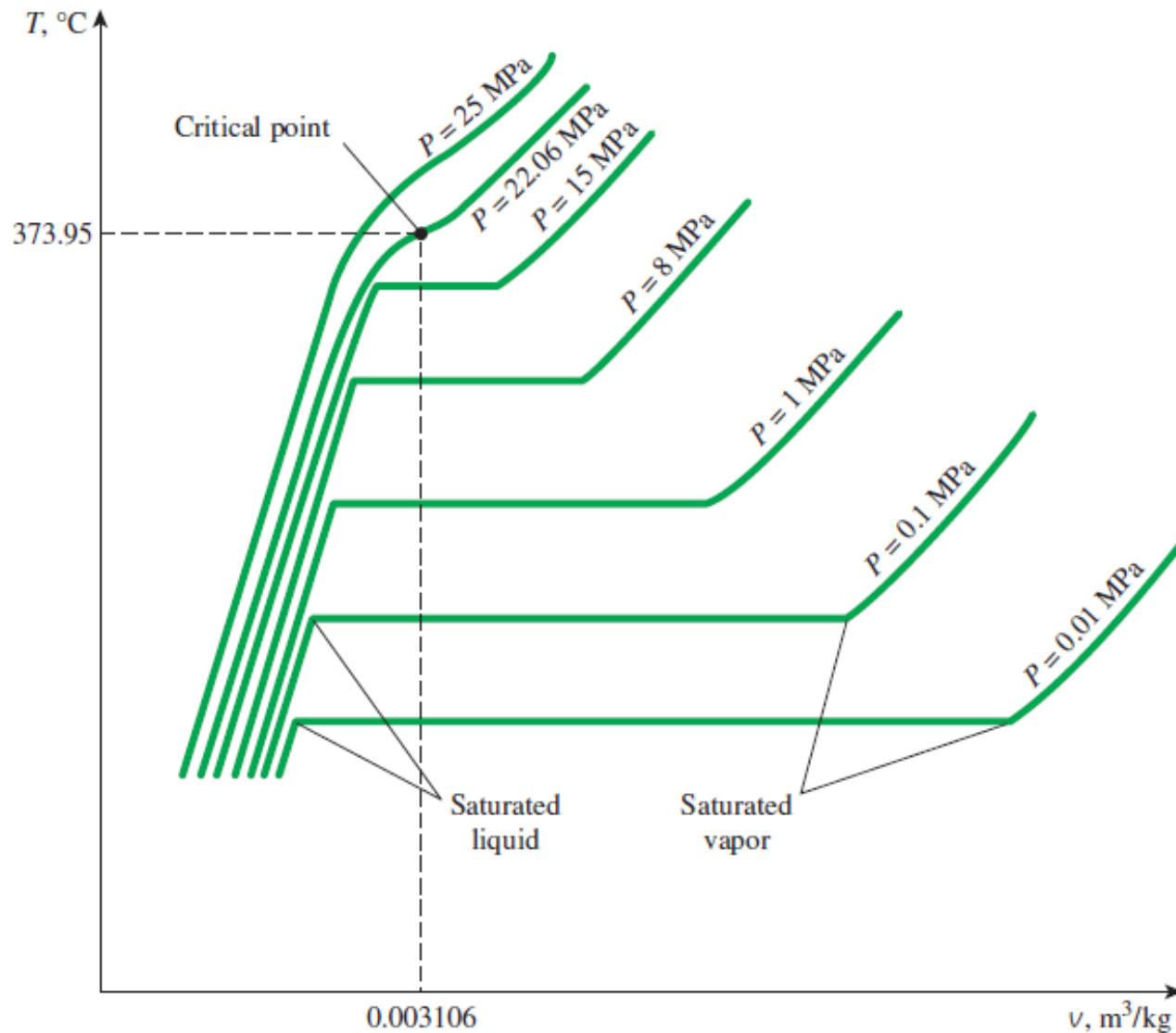
Constant pressure expansion of water :

Note that expansion process of water by heating may be carried out at different (constant) pressures. At 1 atm, $T_{\text{sat}} = 100^\circ\text{C}$. This is the saturation temperature, i.e., the temperature at which liquid \rightarrow vapor transition occurs at constant pressure

It is observed that T_{sat} is uniquely determined by the pressure.

Thus, $T_{\text{sat}} = f(P)$.

Press., P kPa	Sat. temp., T_{sat} $^\circ\text{C}$
101.325	99.97
125	105.97
150	111.35
175	116.04
200	120.21
225	123.97
250	127.41
275	130.58
300	133.52

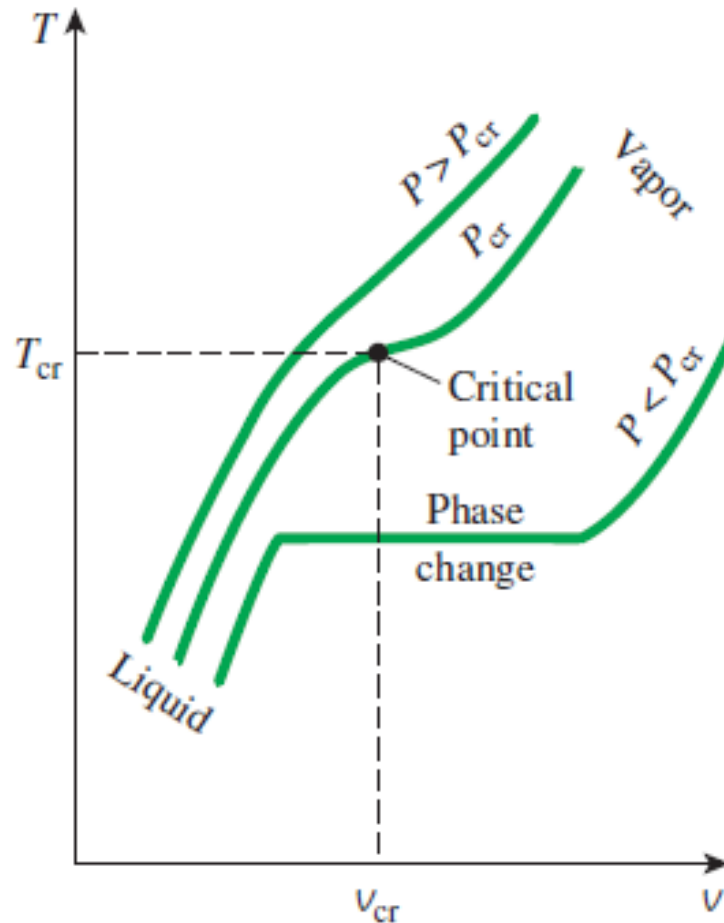


T-v plots resulting from constant pressure expansion of water at various pressures

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

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

Constant pressure expansion :



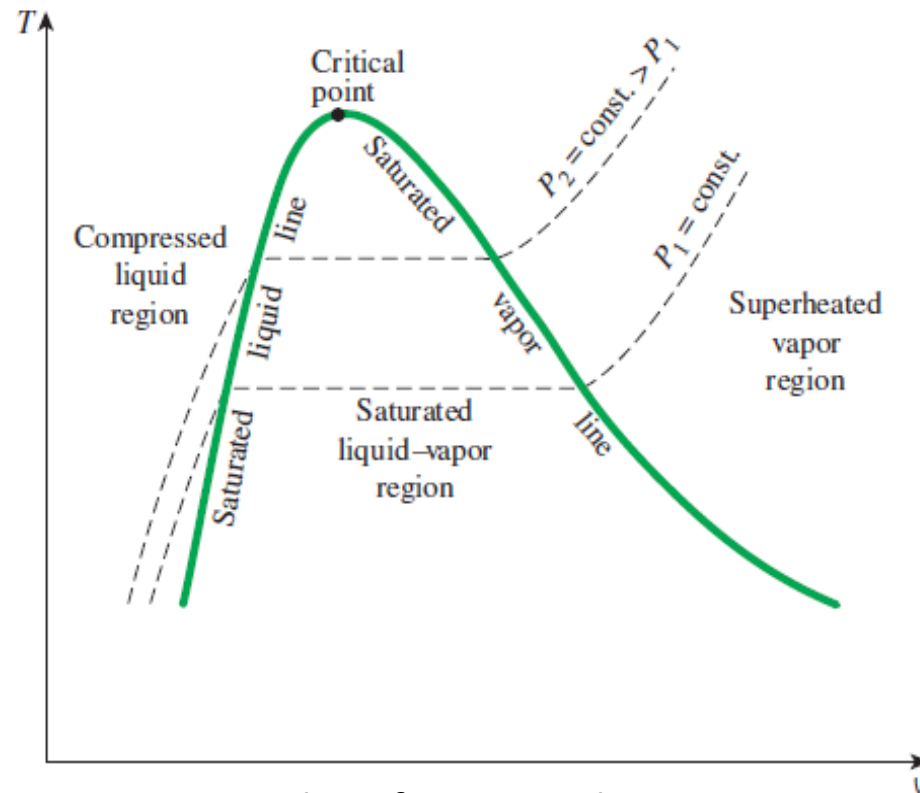
Note that above critical pressure ($P > P_{cr}$), no phase change is observed in constant pressure expansion

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.

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.

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:

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 :

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

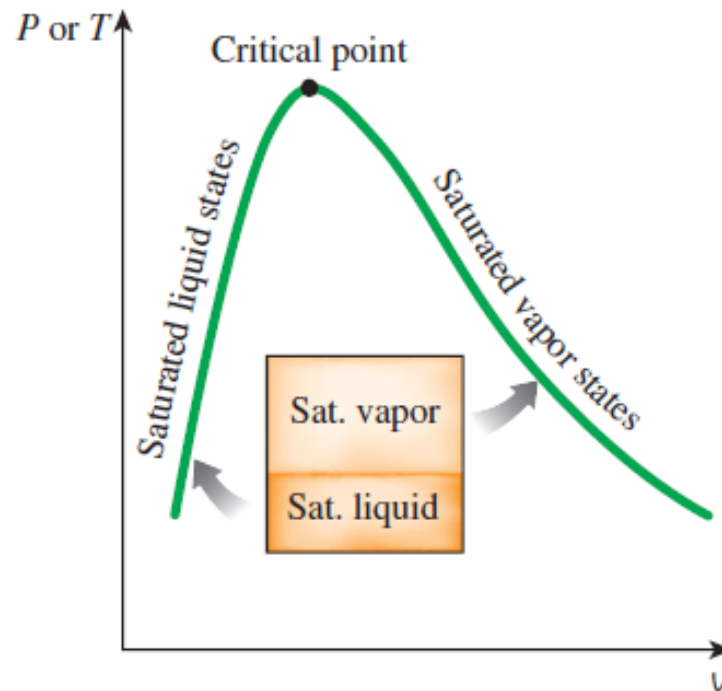
Saturated water—Pressure table												
Press., <i>P</i> kPa	Sat. temp., <i>T</i> _{sat} °C	Specific volume, m ³ /kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg·K		
		Sat. liquid, <i>v</i> _f	Sat. vapor, <i>v</i> _g	Sat. liquid, <i>u</i> _f	Evap., <i>u</i> _{fg}	Sat. vapor, <i>u</i> _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

Constant pressure expansion of water :

For a constant pressure expansion process from 1→2 (see slides 16 and 17)

$$\begin{aligned} Q_{in} (1 \rightarrow 2) &= H_2 - H_1 \\ &= m (h_2 - h_1) \end{aligned}$$

h = specific enthalpy of liquid water (kJ/kg)

m = mass of water (kg)

The quantity $(H_2 - H_1)$ for a change of state from compressed liquid(1) to saturated liquid (2) is called as “**sensible**” heat since temperature increases as a result of providing heat, i.e., water becomes hotter which can be sensed by hand.

Similarly, the quantity $(H_5 - H_4)$ for a change of state from saturated vapor (4) to superheated vapor (5) is also called as “**sensible heat**”

Constant pressure expansion of water :

For the process from 2→4 (slides 16 and 17)

$$\begin{aligned} Q_{in} (2 \rightarrow 4) &= H_4 - H_2 \\ &= m (h_4 - h_2) \\ &= m (h_{g@1atm} - h_{f@1atm}) \end{aligned}$$

h_g = specific enthalpy of saturated vapor (kJ/kg)

h_f = specific enthalpy of saturated liquid (kJ/kg)

The quantity ($H_4 - H_2$) for a change of state from saturated liquid(2) to saturated vapor (2) is called as “**latent**” heat since temperature does NOT change in this process (“latent” means hidden).

The quantity $h_{fg} = (h_g - h_f)$ is the **latent heat of vaporization** in kJ/kg

The values of h_f , h_g , h_{fg} are listed in “steam tables”.