



Chemical Thermodynamics

Chem 211: Lecture 5

Properties of Pure Substances

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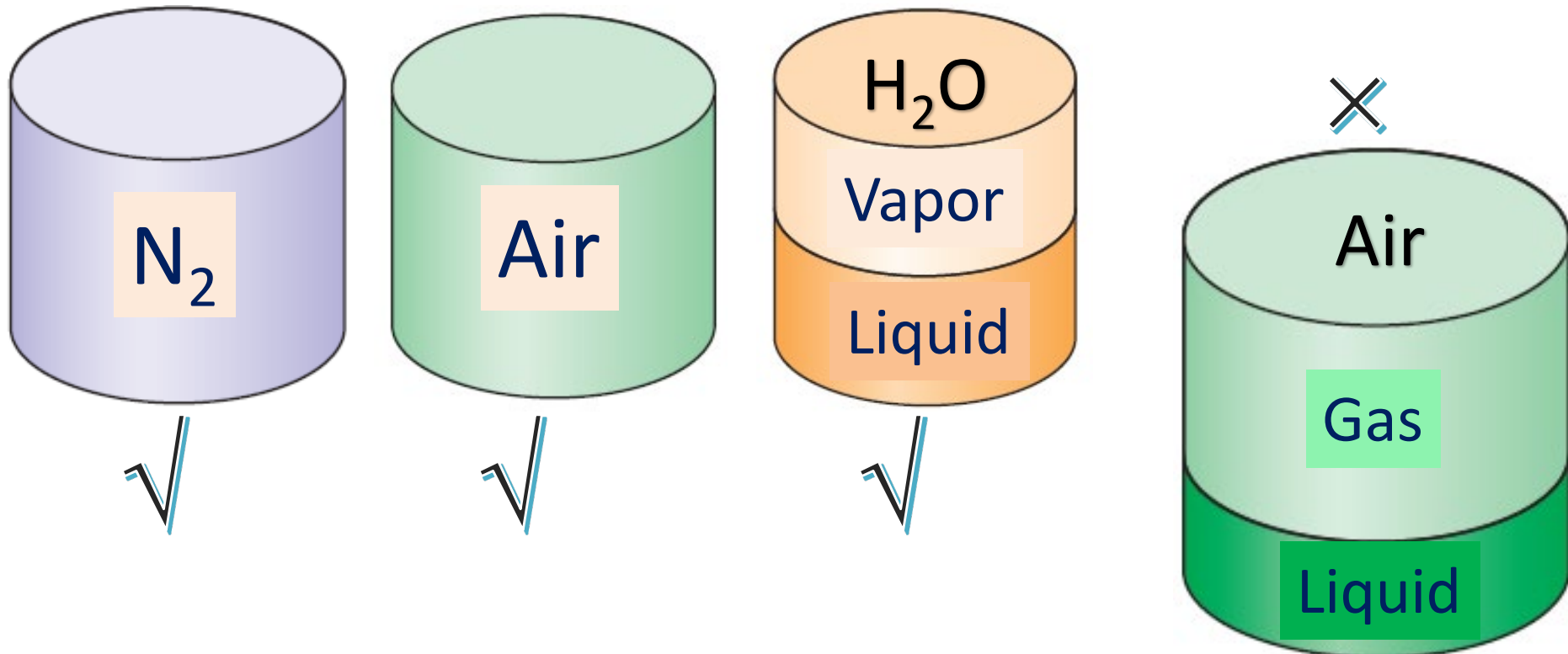
Outline

- Moving boundary work
- States of Matter
- Saturation States
- Property Diagrams
- Superheated Vapor
- Compressed Liquids

Pure Substance

- ✚ a substance that has a **fixed** chemical composition throughout, e.g., water, nitrogen, helium, and carbon dioxide.
- ✚ A **mixture** of various chemical **elements** or **compounds** also qualifies as a pure substance as long as the mixture is **homogeneous**.
- ✚ Air (*in contrast* to oil/water mixture) is a mixture of several gases, but it is often considered to be a pure substance because it has a uniform chemical composition.
- ✚ A mixture of two or more phases of a pure substance (**ice/liq. water**) is still a **pure** substance as long as the chemical composition of all phases is the same.

- ✚ A mixture of liquid air and gaseous air, however, is not a pure substance since the composition of liquid air is **different** from the composition of gaseous air, and thus the mixture is **no longer chemically homogeneous**.
- ✚ This is due to different components in air condensing at different temperatures at a specified pressure.

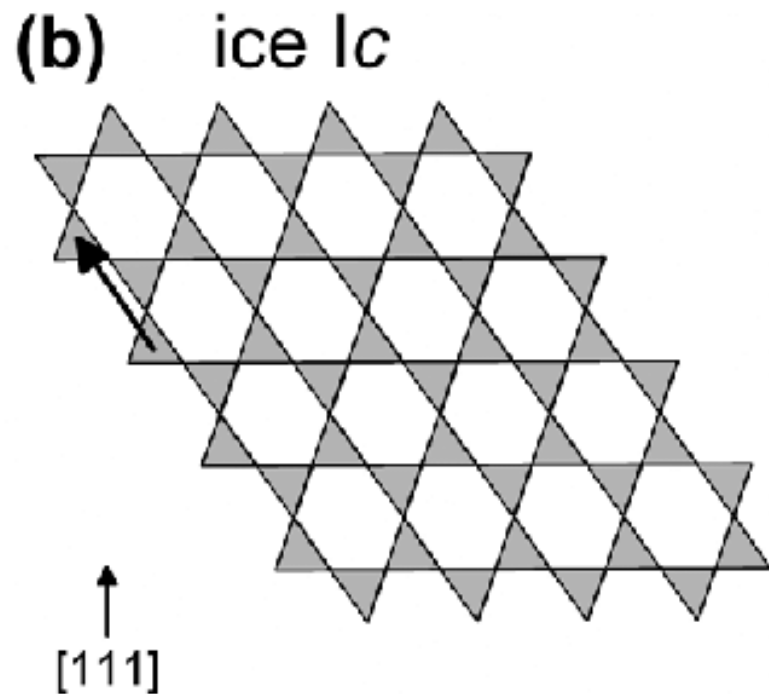
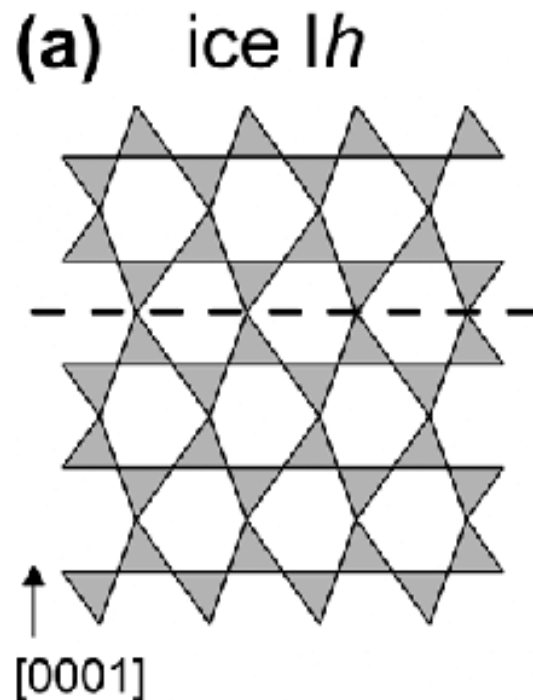


Phases of Pure Substance

- Substances exist in different phases. At room T and P (1 atm), Cu is a solid, Hg is a liquid, and N₂ is a gas.
- Even though there are three principal phases—solid, liquid, and gas—a substance may have several phases within a principal phase, each with a different molecular structure.
- Carbon may exist as graphite or diamond in the solid phase.
- Helium has two liquid phases;
- Iron has three solid phases.
- Ice may exist at seven different phases at high pressures.

✚ A phase is identified as having a **distinct molecular arrangement** that is **homogeneous** throughout and separated from the others by easily identifiable boundary surfaces.

✚ The 2 phases of H_2O in iced water (Ice $I_h \xrightarrow{t < -53^\circ\text{C}} I_c$) is a good example.



States of Matter

Solids

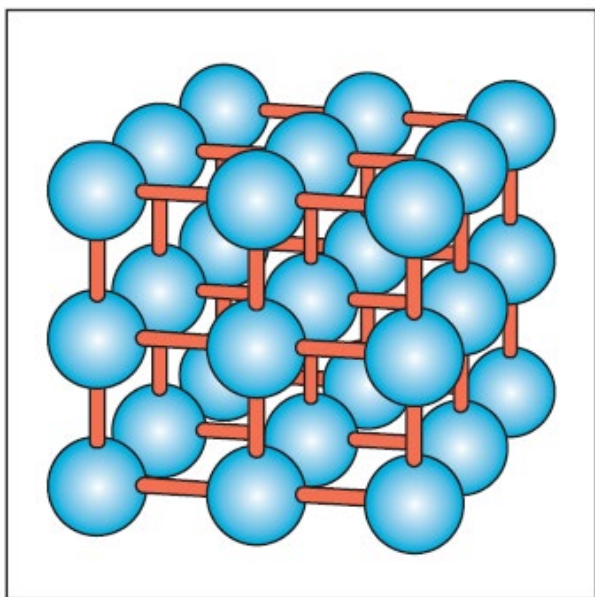
✚ Molecules are arranged in a **repeated 3-D** pattern (**lattice**). Intermolecular distances are **small**, but attractive forces are **large**, keeping molecules at **fixed** positions. Particles have **no translation motions** but continually **oscillate** (depending on T) about their equilibrium positions. At sufficiently high **Ts**, the velocity (and **momentum**) of the molecules may overcome intermolecular forces leading to **melting**.

Liquids

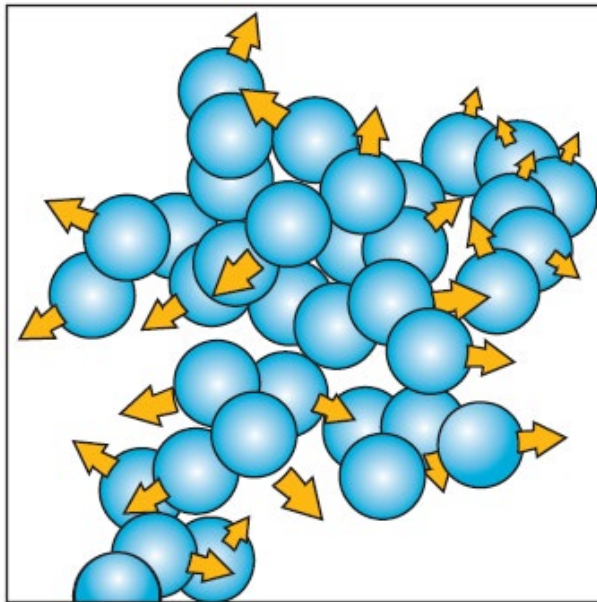
✚ Molecules can **rotate** and **translate** freely. **Intermediate** intermolecular forces. Distances between molecules increase than in solids (**water is an exception**).

Gases

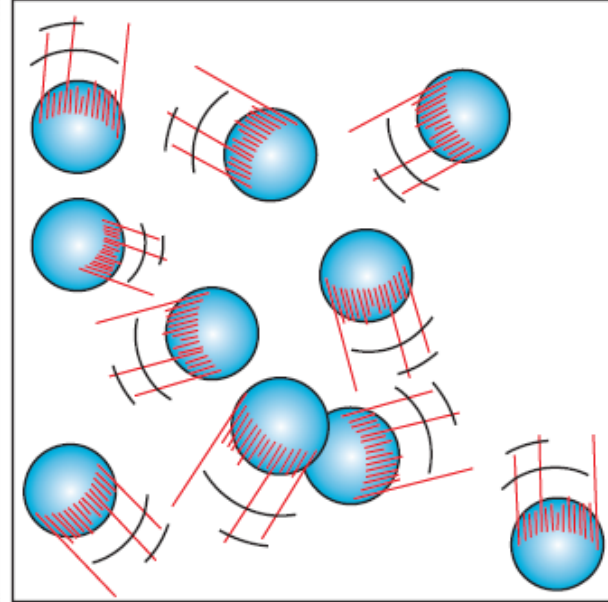
✚ Molecules are **far apart** from each other, no molecular order. Molecules move **randomly**, **continually** colliding with each other and the container's walls. Particularly at **low** densities, the intermolecular forces are very small, and **collisions** are the only mode of interaction between the molecules.



Solids



Liquids

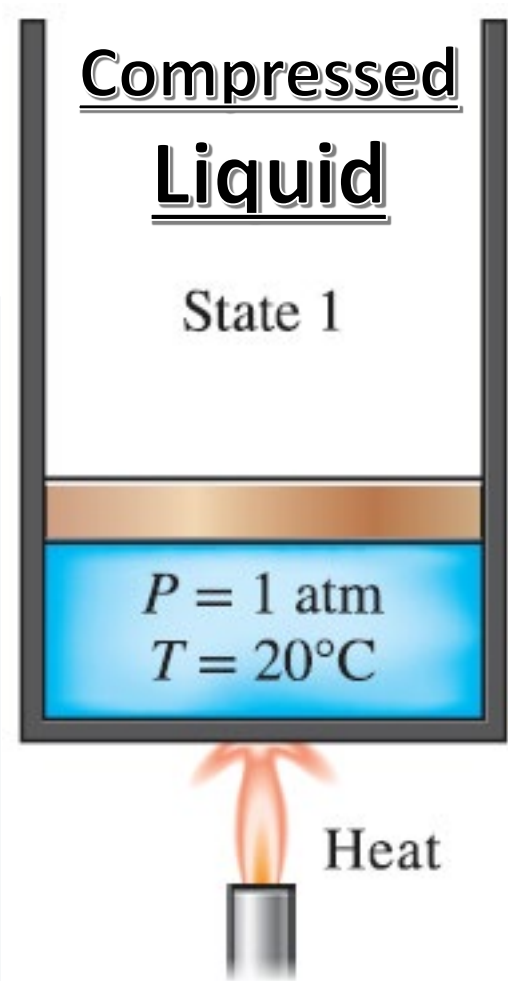


Gases

Phase Changes

Compressed/Saturated Liquids

- Consider a piston–cylinder device containing **liquid** water at 20°C and 1 atm (**state 1**).
- Water exists, herein, in the liquid phase, and it is called a **compressed liquid**, or a **subcooled liquid**, meaning that it is not about to vaporize.



- Heat** is now transferred to the water until its **T** rises to, say, **40°C**. As **T** rises, the liquid water expands slightly, and so its specific volume **increases**. To accommodate this expansion, the piston **moves up** slightly.

✚ P in the cylinder remains **constant** at **1 atm** during this process as it depends on the outside **barometric P** and the **weight of the piston**, both of which are **constant**.

✚ Water is still a **compressed liquid** at this state since it has not started to vaporize.

Saturated Liquid

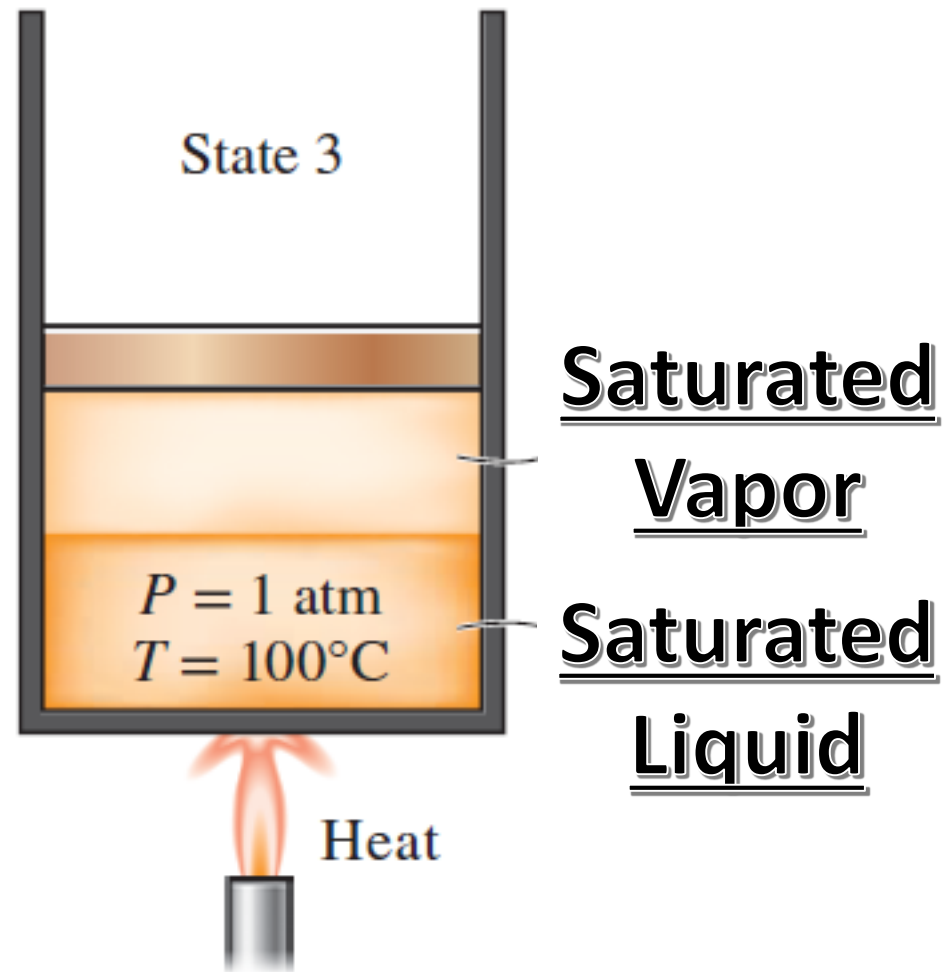
State 2

$P = 1 \text{ atm}$
 $T = 100^\circ\text{C}$



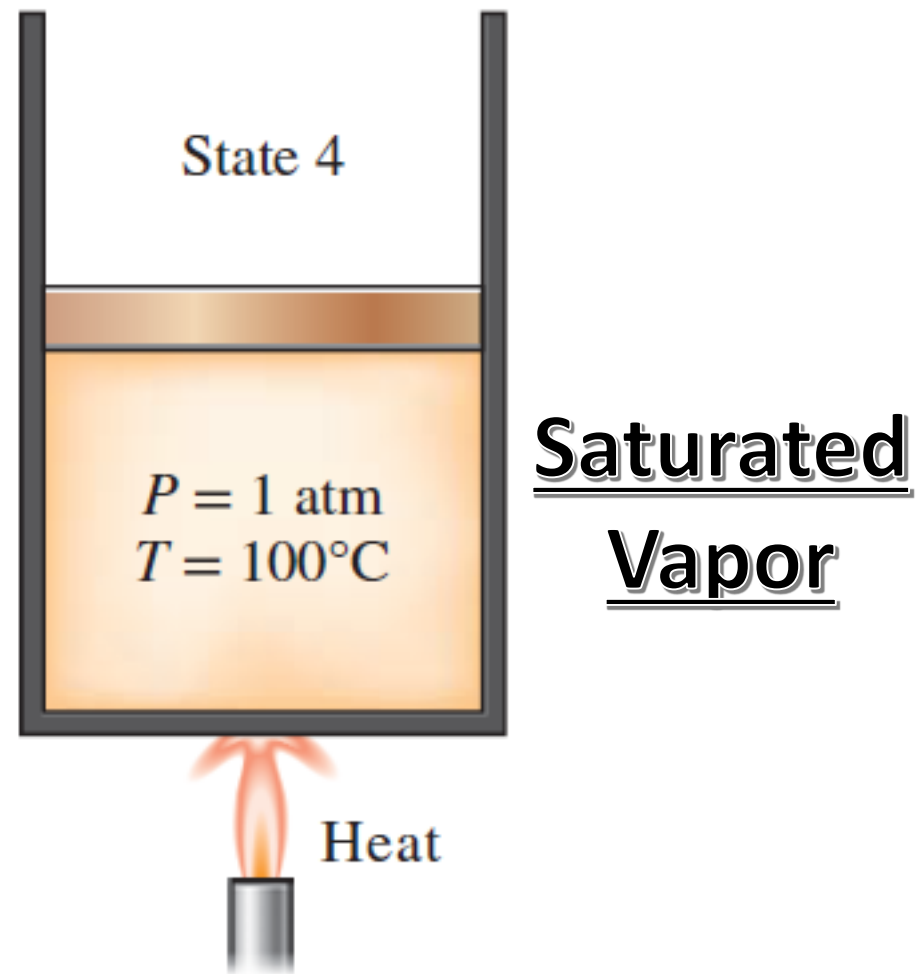
✚ As more heat is added, **T** keeps rising to **100°C** (**state 2**). At this point, water is still a liquid, but any heat addition will cause some of the **liquid** to **vaporize** (a **phase-change** is about to take place). A liquid that is *about to vaporize* is called a **saturated liquid**.

✚ Once boiling starts, the temperature stops rising until the liquid is completely vaporized. That is, the temperature will remain constant during the entire phase-change process if the **pressure** is held **constant**.



- During a **boiling**, a large **increase** in the volume and a steady decline in the liquid level are observed as a result of **more liquid turning to vapor**.

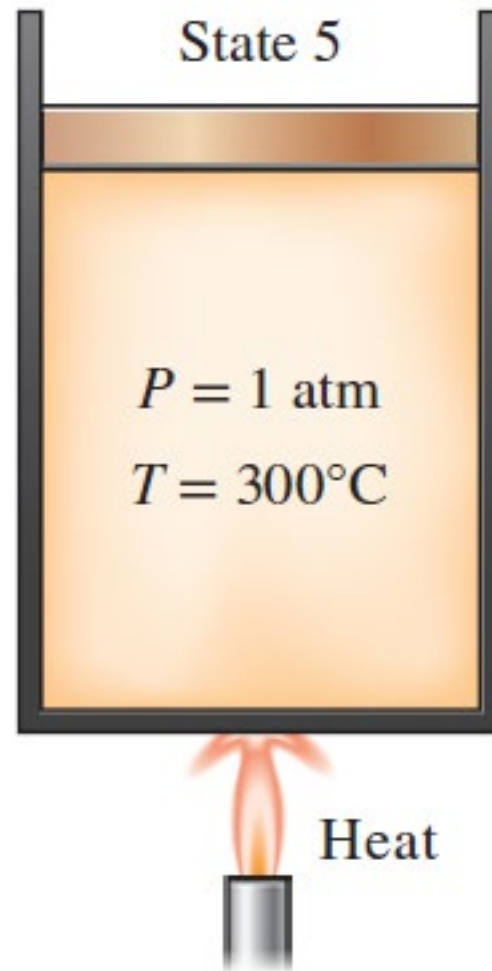
✚ If the last drop of liquid is vaporized, the entire cylinder is filled with **saturated vapor** that is on the borderline of the liquid phase. Any heat loss from this vapor will cause some of the vapor to condense.



✚ A substance at states between 2 and 4 is referred to as a **saturated liquid–vapor** mixture since the liquid and vapor phases coexist in equilibrium at these states.

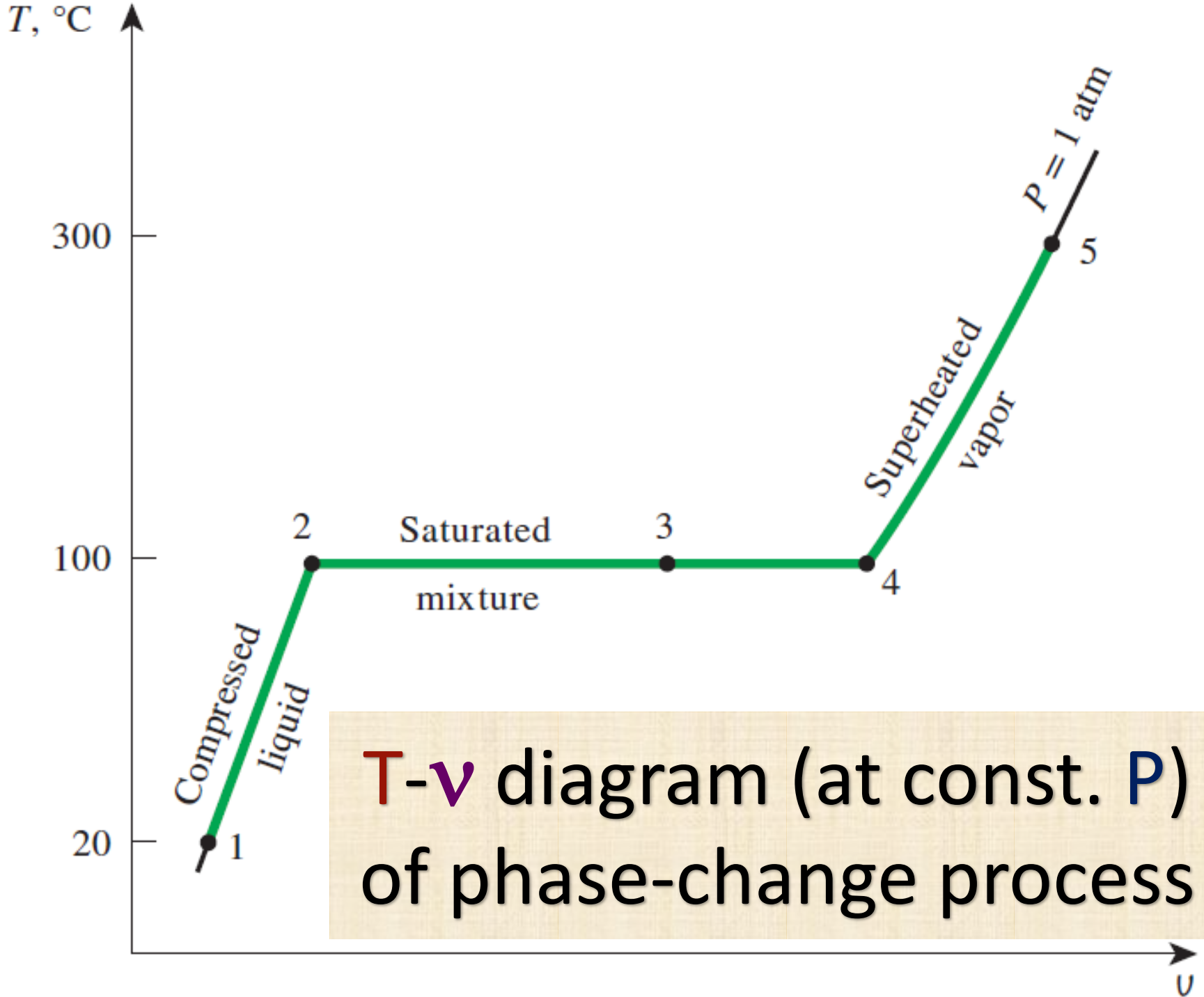
Further transfer of **heat** results in an increase in both T & specific volume.

Removing heat from the vapor may **drop T** somewhat but no condensation will take place as long $T > 100^\circ\text{C}$ (for $P = 1$ atm).



Superheated
Vapor

A vapor that is not about to condense (i.e., not a saturated vapor) is called a **superheated vapor**.

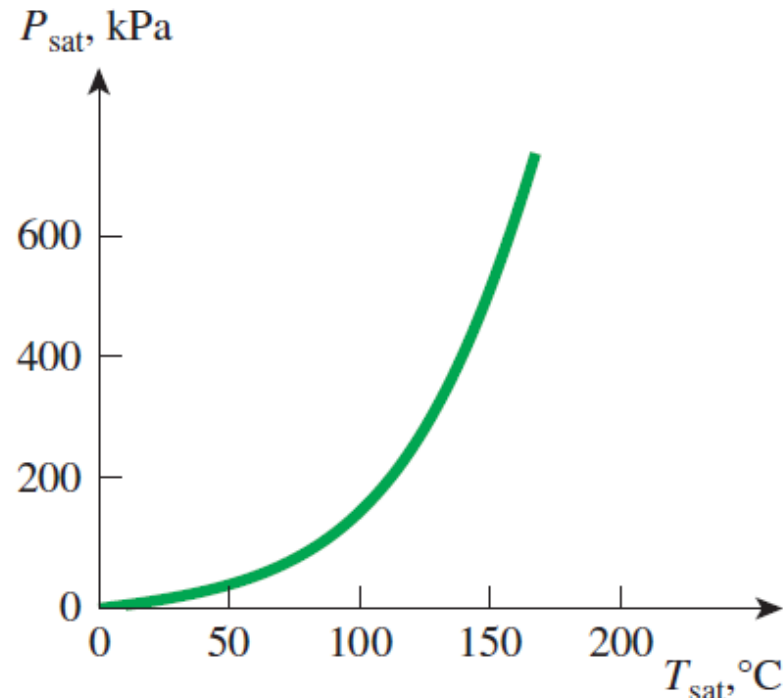


Saturation T & P

- ✚ T at which water starts boiling depends on P ; therefore, if P is fixed, so is the boiling T .
- ✚ At a given P , T at which a pure substance changes phase is called the **saturation temperature** T_{sat} .
- ✚ At a given T , P at which a pure substance changes phase is called the **saturation pressure** P_{sat} .
- ✚ The amount of energy **absorbed** or **released** during a phase-change process is called the **latent heat**, whose magnitude depends on T & P at which the phase change occurs.
- ✚ At 1 atm, latent heat of fusion of water is 333.7 kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.

Liquid-vapor Saturation Curve

- ✚ During a phase-change process, P_{sat} & T_{sat} are obviously dependent with a definite relation $P_{\text{sat}} = f(T_{\text{sat}})$.
- ✚ A substance at higher P_{sat} boils at higher T_{sat} .
- Higher T_{sat} means shorter cooking times and energy savings. A **beef stew**, taking 2 h to cook in a regular pan (at 1 atm), only takes 20 min in a pressure cooker (3 atm) (corresponding T_{boil} 134°C).

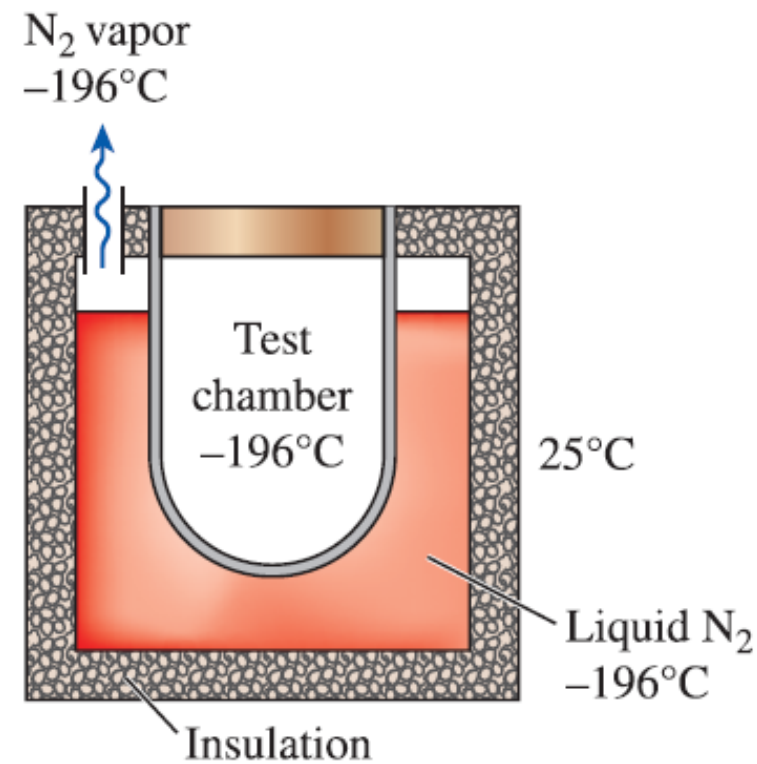


Liquid–vapor saturation curve of a pure substance (numerical values are for water).

it takes **longer** to cook at **higher** altitudes than it does at sea level

Liquid N_2

- ✚ T_{boil} of N_2 at $P_{\text{atm}} = -196^\circ\text{C}$.
- ✚ T of liquid N_2 remains constant at -196°C , until it is depleted.
- ✚ N_2 is commonly used in low- T applications to maintain a test chamber at a constant T of -196°C by placing the test chamber into a liquid N_2 bath that is open to the atmosphere.

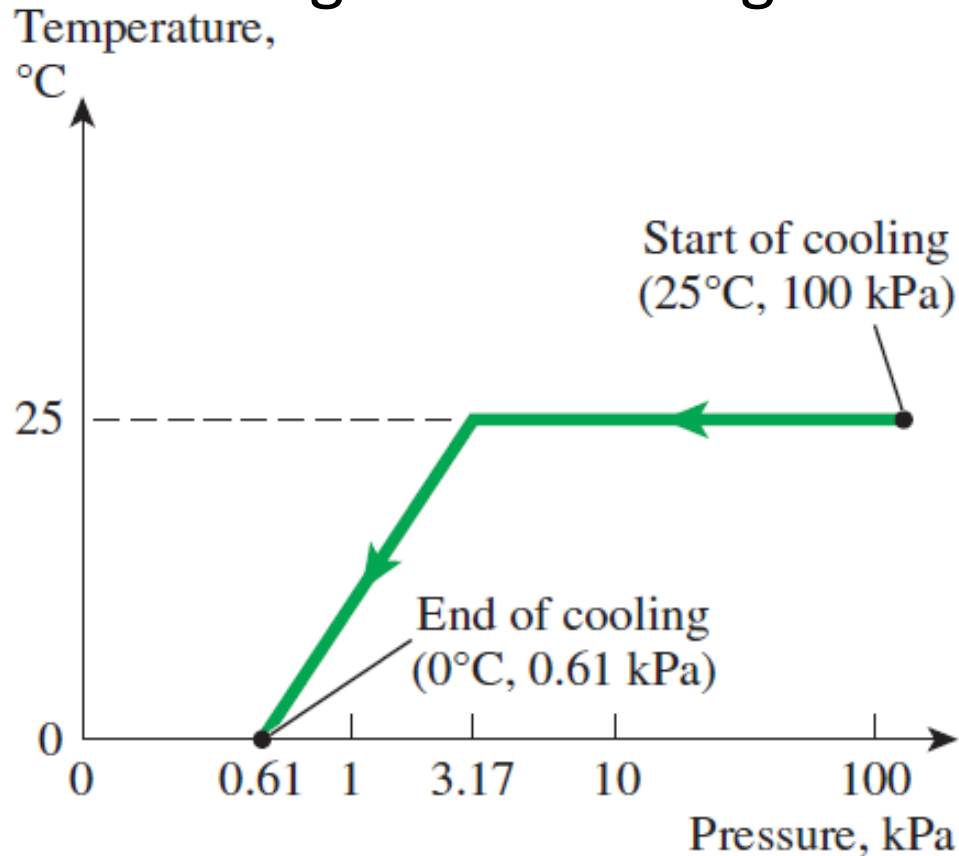


Any heat transfer from the environment to the test section is absorbed by N_2 , which evaporates isothermally and keeps the chamber T constant at -196°C

Vacuum Cooling

- ✦ A practical way of cooling leafy vegetables is based on reducing P of the sealed cooling chamber to P_{sat} at the desired low T and evaporating some water from the products to be cooled.
- ✦ ΔH_{vap} is absorbed from the products, which lowers the product T .
- ✦ The products at 25°C , are loaded into the chamber, and this T remains constant until the P_{sat} is reached, which is **3.17** kPa at **25°C**.
- ✦ Saturation conditions are maintained inside at progressively *lower* P_{sat} and the corresponding *lower temperatures* T until the desired T is reached.

VC: is more expensive but *much faster* than conventional refrigerated cooling



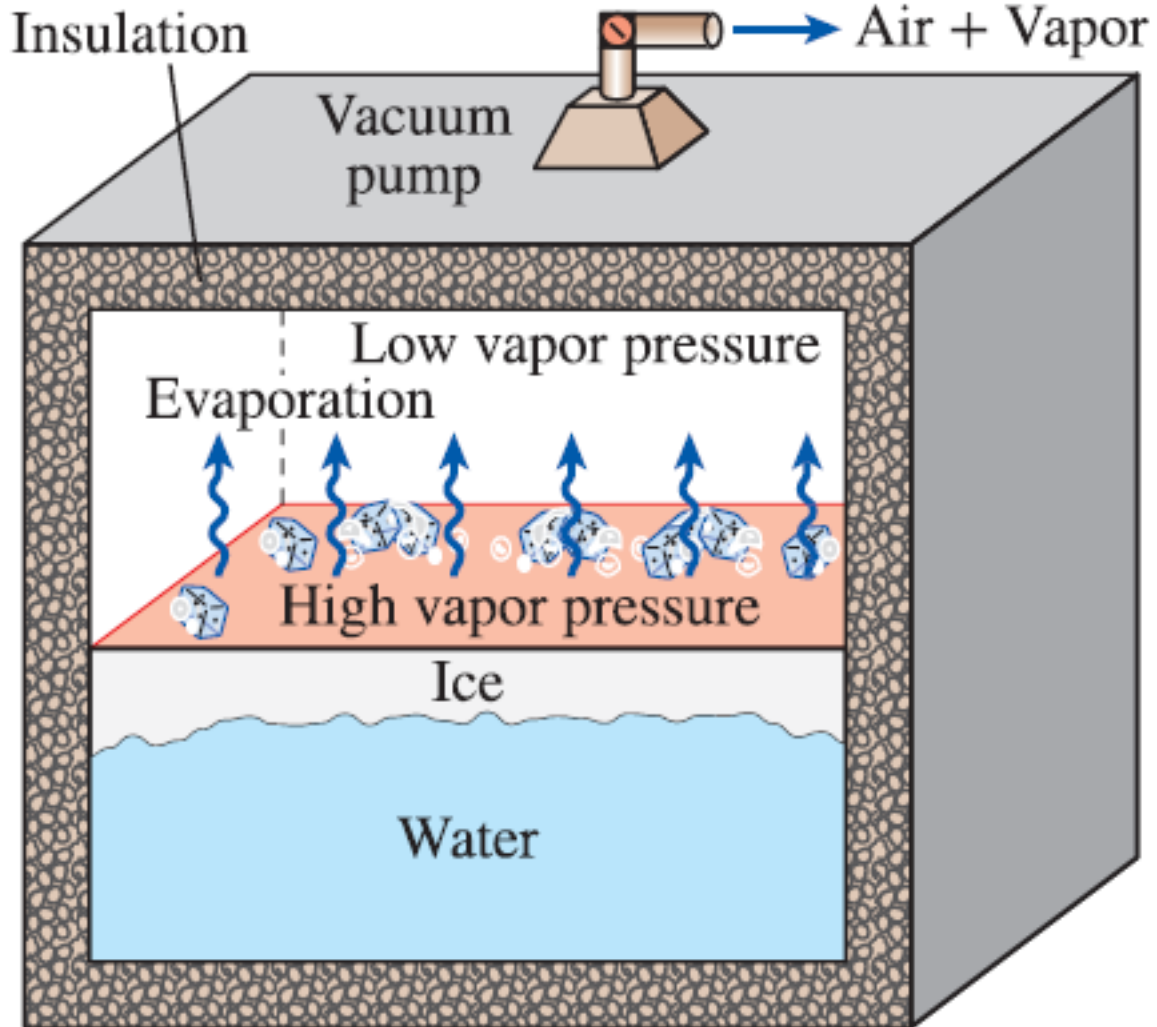
Saturation (or vapor) pressure of water at various temperatures

Temperature $T, ^\circ\text{C}$	Saturation pressure $P_{\text{sat}}, \text{kPa}$
-10	0.260
-5	0.403
0	0.611
5	0.872
10	1.23
15	1.71
20	2.34
25	3.17
30	4.25
40	7.38
50	12.35
100	101.3 (1 atm)
150	475.8
200	1554
250	3973
300	8581

✚ Products with large surface area per unit mass and a high tendency to release moisture such as lettuce الخس & spinach السبانخ are well suited for vacuum cooling

Vacuum Freezing

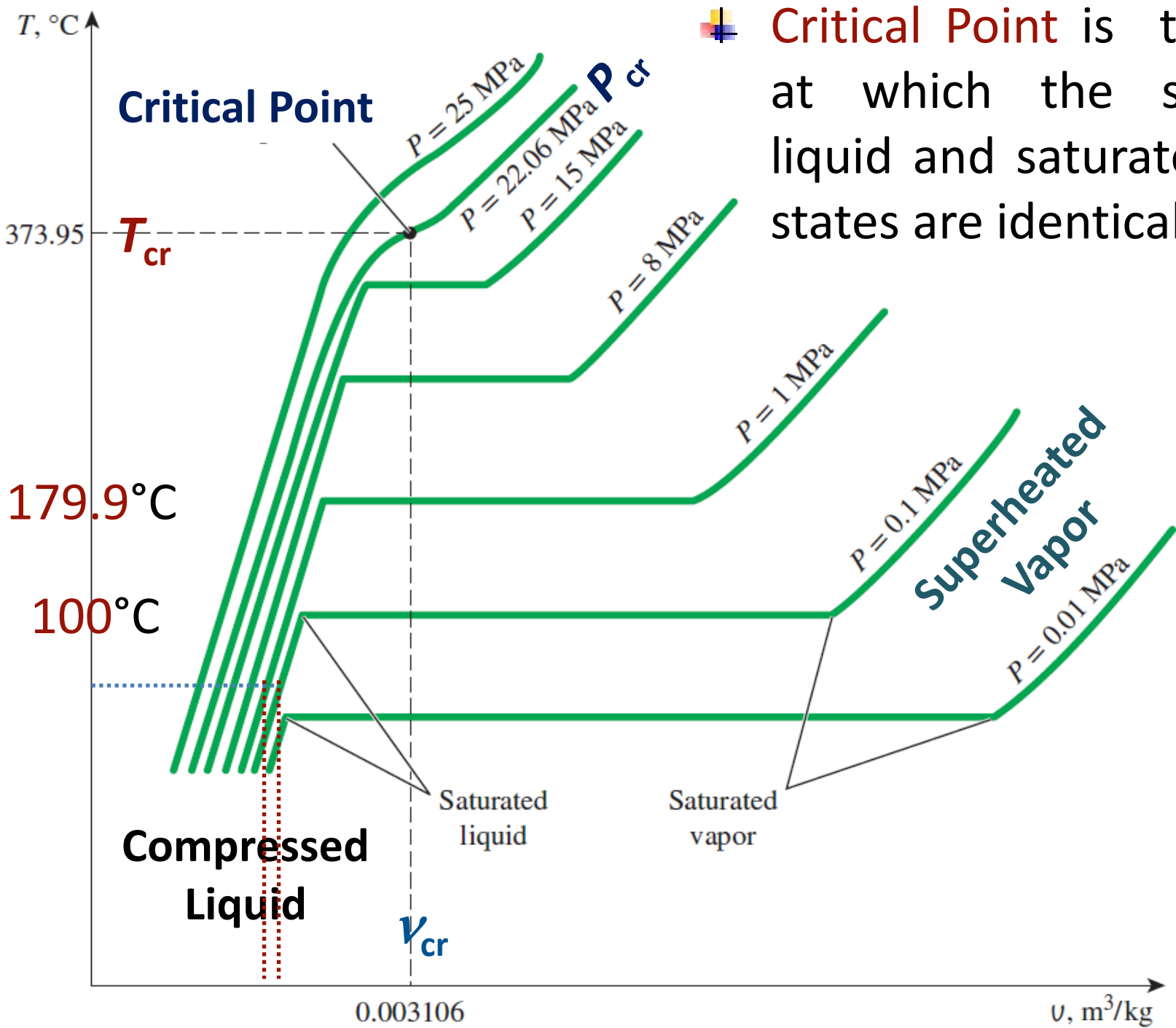
is achieved if the vapor P in the vacuum chamber is dropped below **0.61** kPa, the P_{sat} of water at 0°C . (**Triple point** of water is **0.01** $^{\circ}\text{C}$ and **611.73** Pa).




Dr. **William Cullen** made **ice** in Scotland in **1775** by evacuating the air in a water tank.

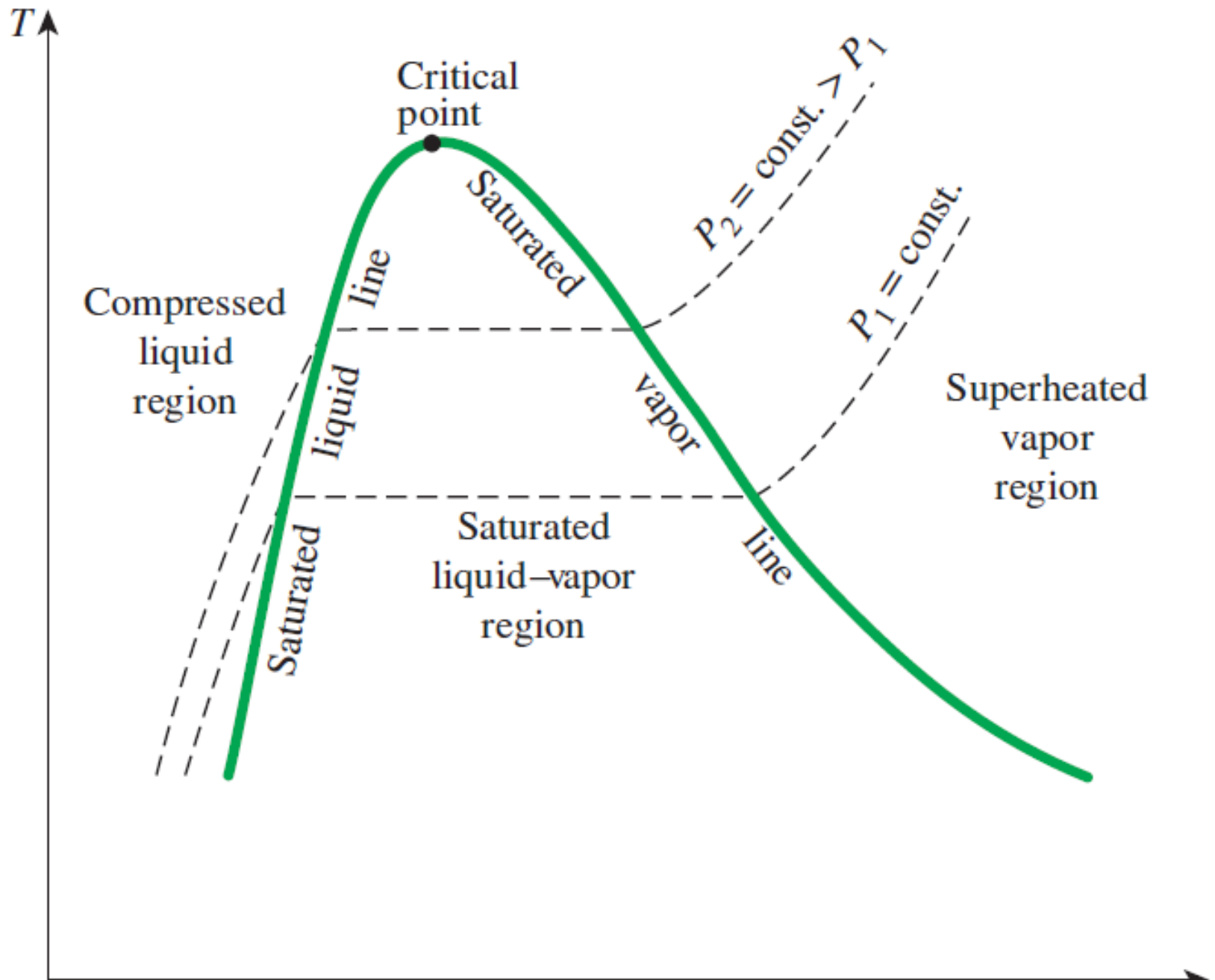
T - v Property diagrams

- concern with variations of **properties** during **phase-change** processes.
- For water at **1 MPa**, liquid water has a somewhat smaller v than it does at **1 atm**. It starts boiling at a much higher T (**179.9°C**). v of sat. liquid is larger and v of sat. vapor is smaller than corresponding values at **1 atm**, *i.e.*, horizontal line connecting saturated liquid and saturated vapor states is much shorter.
- As **P** is increased further, this saturation line continues to **shrink**, and it becomes a point when the pressure reaches **22.06 MPa** for the case of water (**Critical point**).




Critical Point is the point at which the saturated liquid and saturated vapor states are identical.

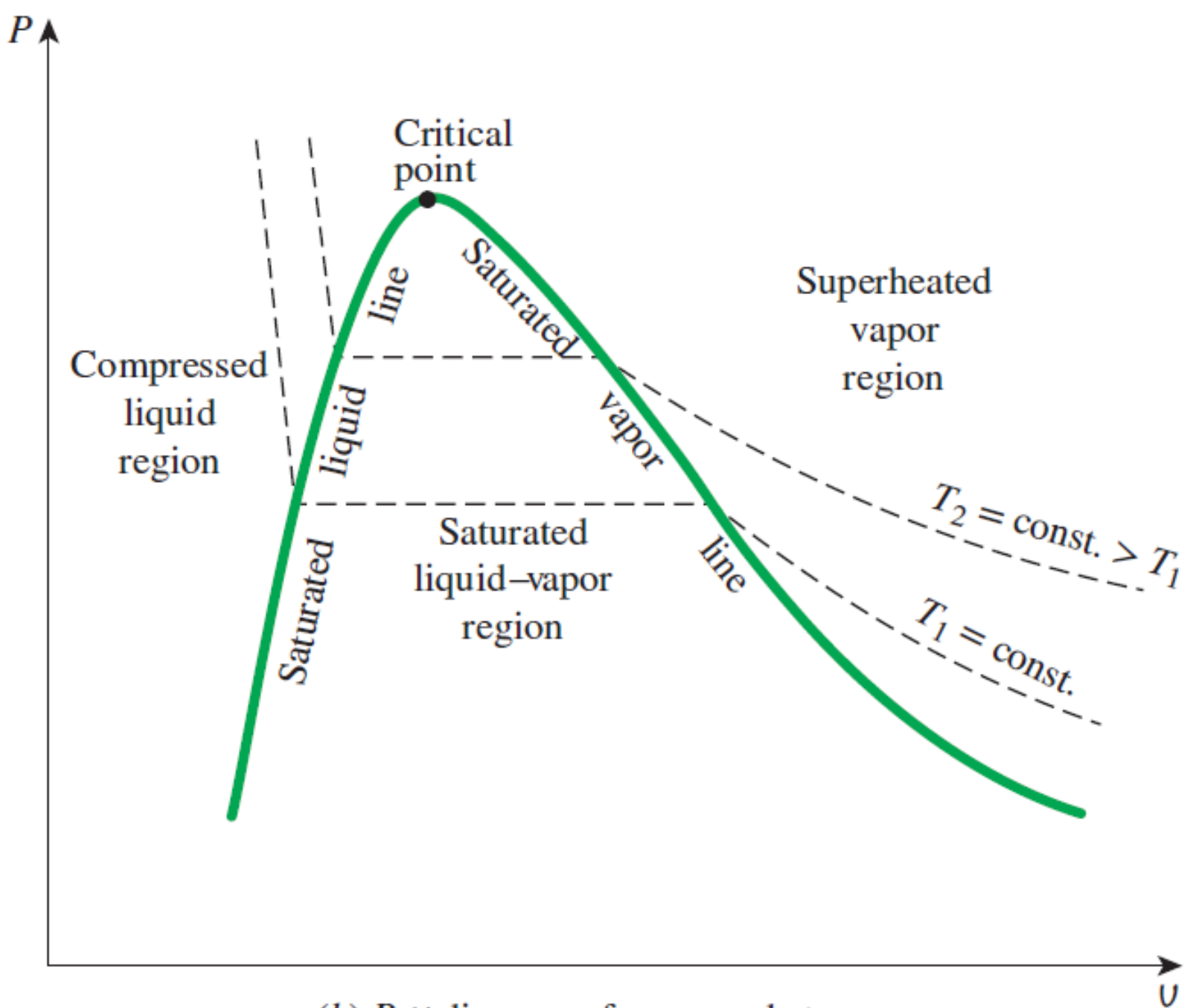
- ✚ Above P_{cr} , there is not a **distinct** phase-change process. Instead, v continually increases, and always there is only **one phase** present. There is **no line** that separates the **compressed liquid** region and **superheated vapor** region.
- ✚ Connection of **saturated liquid** & **saturated vapor** lines meet at **critical point**, forming a **dome**.
- ✚ The **compressed liquid region** (or subcooled liquid region) is in the region to **left** of saturated liquid line.
- ✚ The **superheated vapor region** is located to the right of the saturated vapor line.
- ✚ All the states that involve both phases in equilibrium are located under the dome, called the **saturated liquid–vapor mixture region**, or the **wet region**.



(a) T - v diagram of a pure substance

P - v Property diagram

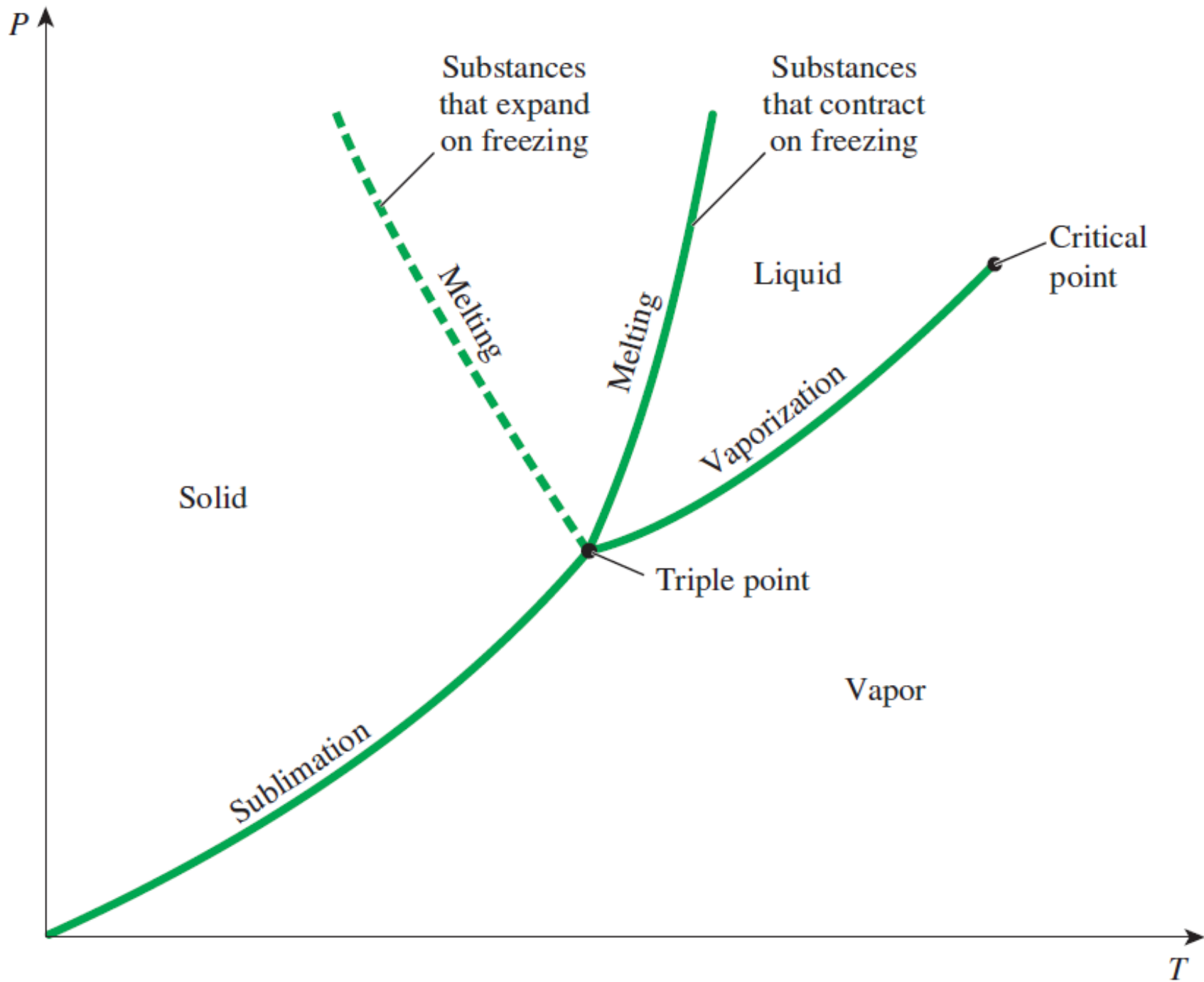
- + Consider a piston–cylinder device that contains **compressed liquid water** at **1 MPa** and **150°C**.
- + If P decreases gradually, (while water is allowed to exchange heat with the surroundings to maintain a const. T for water) v will increase slightly.
- + When P_{sat} (**0.4762 MPa**) attains at **150°C**, water starts to boil and both of T and P remain constant but v increases.
- + Once the last drop of liquid is vaporized, further reduction in P results in a further increase in v .
- + What may happen if P decreased during the phase-change process? (Process is no longer **isothermal**)



(b) P - v diagram of a pure substance

P - T Property diagram

- ✚ is often called the **phase diagram** since all three phases are separated from each other by three lines of **sublimation**, **vaporization** and **melting** (or **fusion**).
- ✚ These three lines meet at the triple point, where all three phases coexist in **equilibrium**.
- ✚ The vaporization line ends at the **critical point** because no distinction can be made between liquid and vapor phases above the critical point.
- ✚ Substances that **expand** and **contract** on freezing differ only in the melting line on the P - T diagram.



Property Tables

✚ A rigid tank contains 50 kg of saturated liquid water at 90°C. Determine the pressure in the tank and the volume of the tank.

Answer

$$P = P_{\text{sat}} @ 90^\circ\text{C}. = 70.183 \text{ kPa}$$

$$v = v_f @ 90^\circ\text{C}. = 0.001036 \text{ m}^3/\text{kg}$$

$$V = mv = (50 \text{ kg})(0.001036 \text{ m}^3/\text{kg}) = 0.0518 \text{ m}^3$$

Temp. °C T	Sat. press. kPa P_{sat}	Specific volume m^3/kg	
		Sat. liquid v_f	Sat. vapor v_g
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

↑
Temperature

↑
Specific volume of saturated liquid

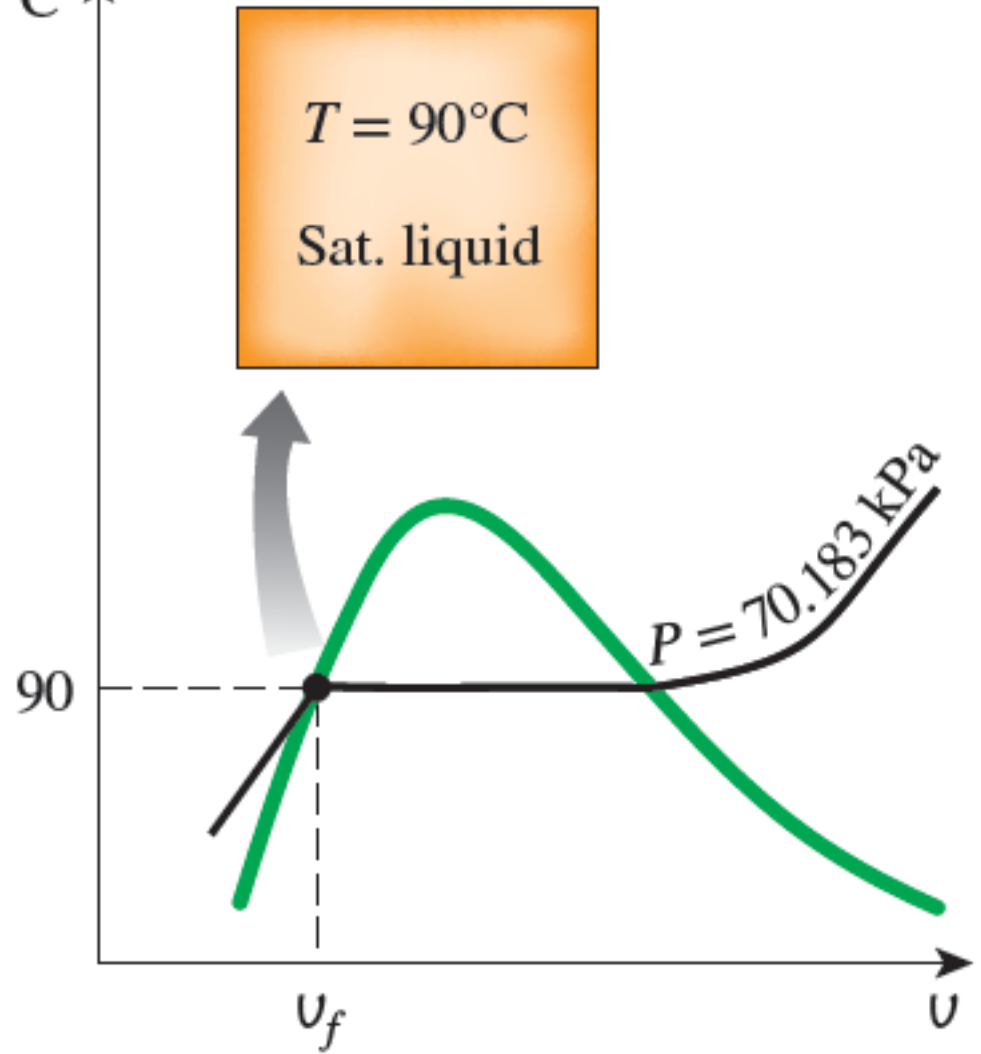
↑
Corresponding saturation pressure

↑
Specific volume of saturated vapor

$T, ^\circ\text{C}$

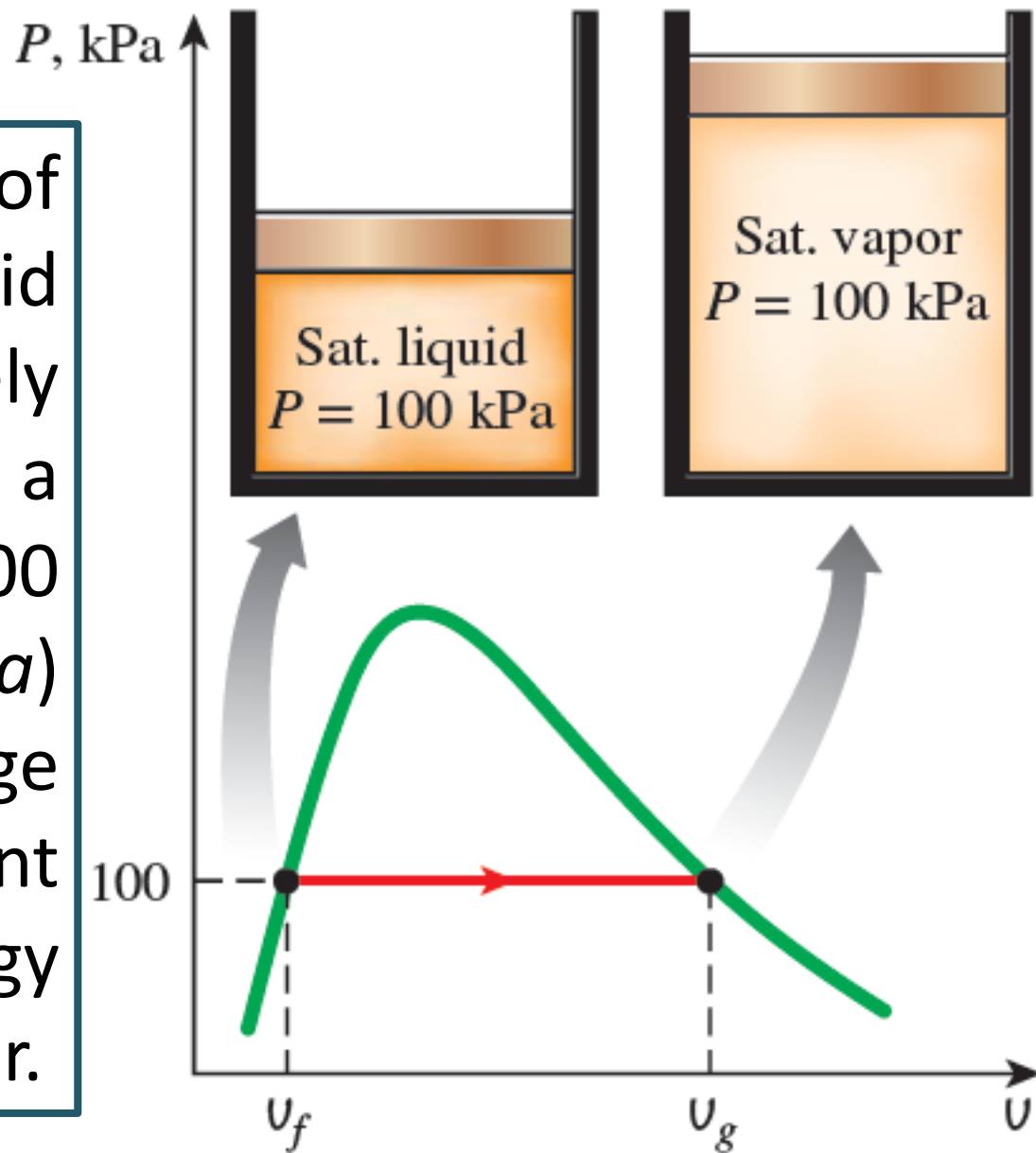
The state of the saturated liquid water is shown on a $T-v$ diagram.

Since saturation conditions exist in the tank, the pressure must be the saturation pressure at 90°C .



Example

A mass of 200 g of saturated liquid water is completely vaporized at a constant P of 100 kPa. Determine (a) the volume change and (b) the amount of energy transferred to water.



Answer

TABLE A-5

Saturated water—Pressure table

Press., <i>P</i> kPa	Sat. temp., T_{sat} °C	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
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
75	91.76	0.001037	2.2172	384.36	2111.8	2496.1	384.44	2278.0	2662.4	1.2132	6.2426	7.4558
100	99.61	0.001043	1.6941	417.40	2088.2	2505.6	417.5	2257.5	2675.0	1.3028	6.0562	7.3589
101.325	99.97	0.001043	1.6734	418.95	2087.0	2506.0	419.06	2256.5	2675.6	1.3069	6.0476	7.3545

The volume change per unit mass during a vaporization process is v_{fg}

$$v_{fg} = v_g - v_f = 1.6941 - 0.001043 = 1.6931 \text{ m}^3/\text{kg}$$

Observe significant figures

$$\Delta v = m v_{fg} = (0.2 \text{ kg})(1.6931 \text{ m}^3/\text{kg}) = 0.3386 \text{ m}^3$$

✚ Combination of properties $u + Pv$ is defined as a new property, **enthalpy**, and given the symbol h :

$$h = u + Pv \quad (kJ/kg)$$

$$H = U + PV \quad (kJ)$$

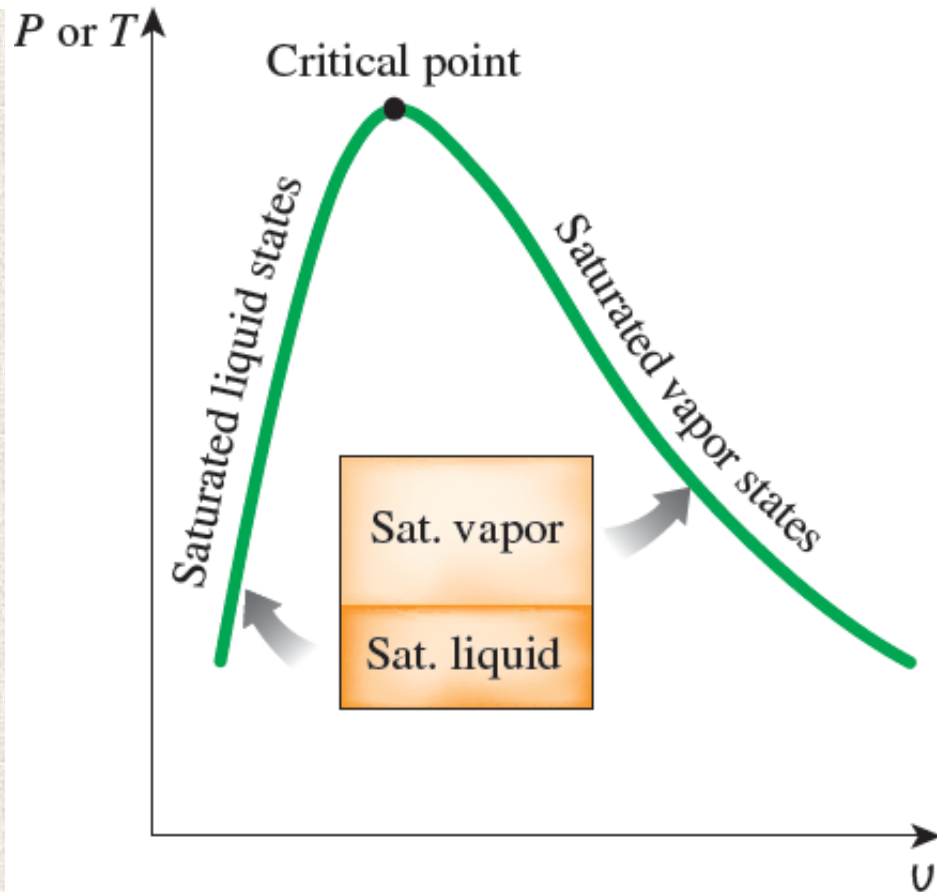
✚ The amount of energy needed to vaporize a unit mass of a substance at a given pressure is the enthalpy of vaporization at that pressure, which is $h_{fg} = 2257.5$ kJ/kg for water at 100 kPa. Thus, the amount of energy transferred is:

$$mh_{fg} = (0.2 \text{ kg})(2257.5 \text{ kJ/kg}) = 451.5 \text{ kJ}$$

Saturated Liquid–Vapor Mixture

During **vaporization**, a substance exists as part **liquid** and part **vapor**, i.e., a mixture of **saturated liquid** and **saturated vapor**.

We need to know the proportions of the **liquid** and **vapor** phases in the mixture. A new property called the **quality** x is defined as the *ratio of the mass of vapor to the total mass of the mixture*.



$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}}$$

$$\begin{aligned} m_{\text{total}} &= m_{\text{liquid}} + m_{\text{vapor}} \\ &= m_f + m_g \end{aligned}$$

- + x has significance for *saturated mixtures* only.
- + x varies between 0 or 0% (for *saturated liquid*) and 1 or 100% (for *saturated vapor*).
- + In saturated mixtures, x can serve as one of the two independent intensive properties needed to describe a state. Note that *the properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapor*.
- + During *vaporization*, only the amount of saturated liquid changes, not its properties. The same can be said about a *saturated vapor*.

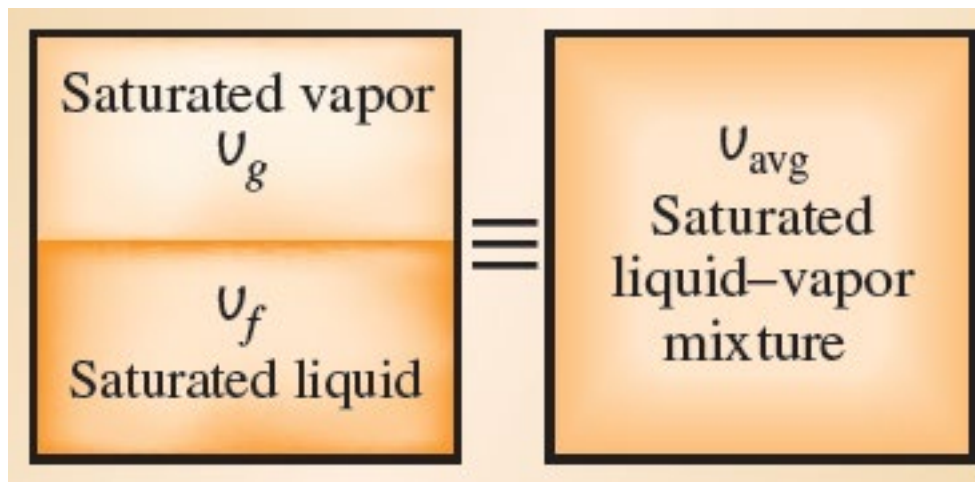
- A saturated mixture can be treated as a combination of two subsystems: the saturated liquid and the saturated vapor of unknown masses.
- It is often more convenient to imagine that the two phases are mixed well, forming a homogeneous mixture whose properties will simply be the average properties of the saturated liquid–vapor mixture

$$V = V_f + V_g$$

$$V = m v$$

$$m_t v_{\text{avg}} = m_f v_f + m_g v_g$$

$$m_f = m_t - m_g$$



$$m_t v_{\text{avg}} = (m_t - m_g) v_f + m_g v_g$$

$$m_t v_{\text{avg}} = (m_t - m_g) v_f + m_g v_g$$

Divide by m_t

$$v_{\text{avg}} = (1 - x) v_f + x v_g$$

$$v_{\text{avg}} = v_f - x v_f + x v_g$$

$$v_{\text{avg}} = v_f + x(v_g - v_f)$$

$$v_{\text{avg}} = v_f + x v_{fg} \quad (m^3/kg)$$

$$x = \frac{(v_{\text{avg}} - v_f)}{v_{fg}}$$

as $x = m_g/m_t$

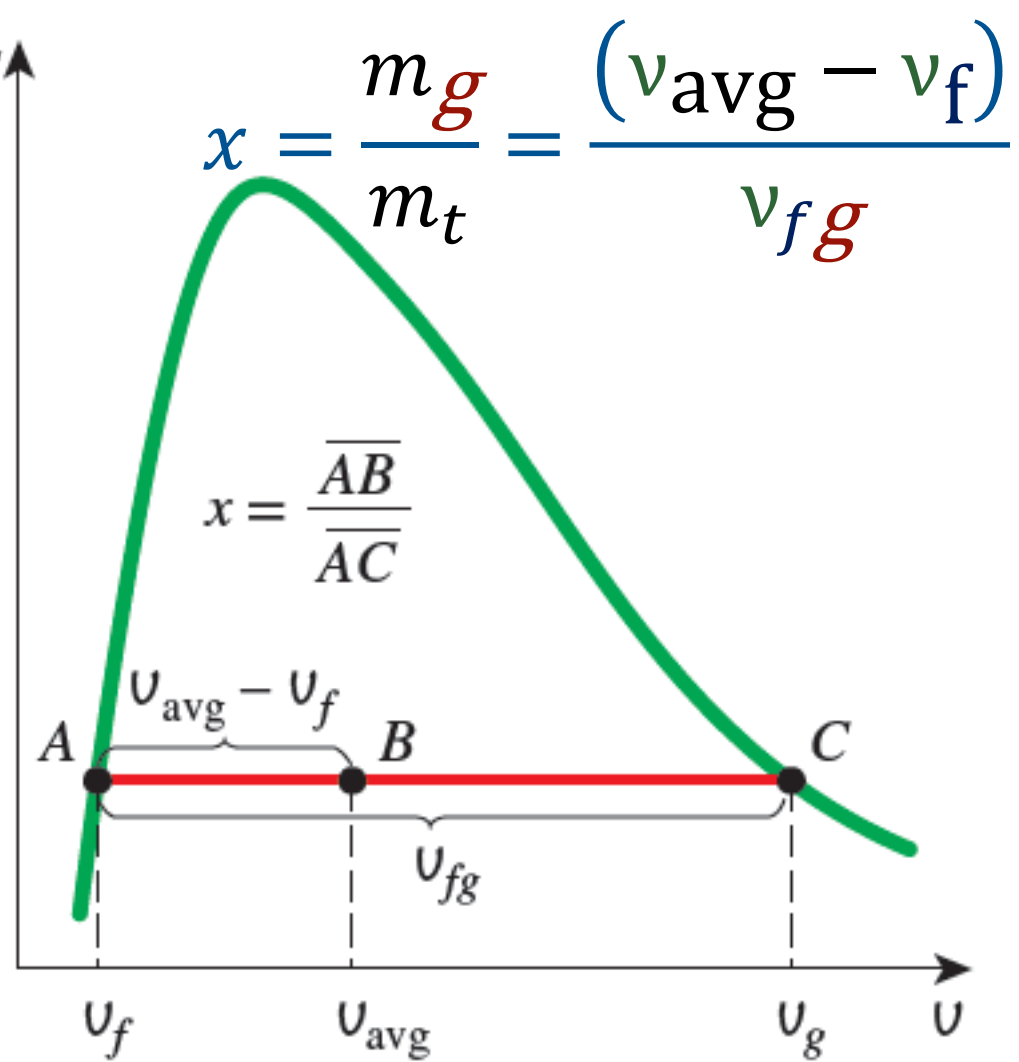
$$x = \frac{m_g}{m_t} = \frac{(v_{\text{avg}} - v_f)}{v_{fg}}$$

✚ quality can be related to the horizontal distances on a $P-v$ or $T-v$ diagram.

✚ A state of 50% quality lies in the middle of this horizontal line.

✚ Same analysis can be repeated for internal energy and enthalpy.

P or T ↑



$$u_{\text{avg}} = u_f + x u_{fg} \quad (\text{kJ/kg})$$

$$h_{\text{avg}} = h_f + x h_{fg} \quad (\text{kJ/kg})$$

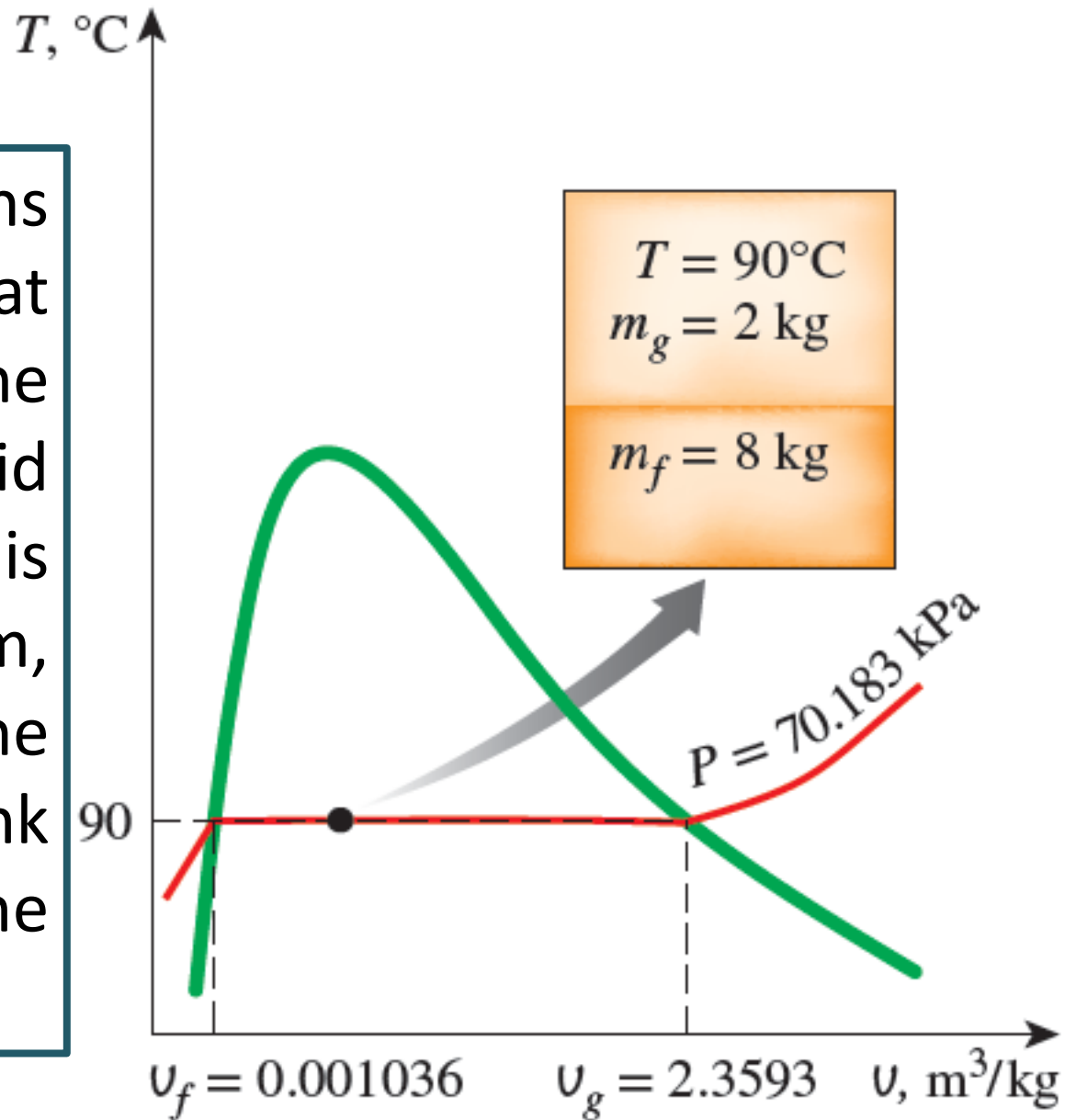
Generally, $y_{\text{avg}} = y_f + xy_fg$ $y = v, u \text{ or } h$

- ✚ The subscript “avg” (for “average”) is usually dropped for simplicity.
- ✚ The values of the **average** properties of the mixtures are always *between* the values of the **saturated liquid** and the **saturated vapor** properties.

$$y_f \leq y_{\text{avg}} \leq y_g$$

Example

A rigid tank contains 10 kg of water at 90°C. If 8 kg of the water is in the liquid form and the rest is in the vapor form, determine (a) the pressure in the tank and (b) the volume of the tank.



Answer

$$P = P_{\text{sat @90}^\circ\text{C.}} = 70.183 \text{ kPa}$$

$$V = V_f + V_g = m_f v_f + m_g v_g$$

$$= (8 \text{ kg})(0.001036 \text{ m}^3/\text{kg}) + (2 \text{ kg})(2.3593 \text{ m}^3/\text{kg})$$
$$= 4.73 \text{ m}^3$$

Alternatively,

$$x = \frac{m_g}{m_t} = \frac{2 \text{ kg}}{10 \text{ kg}} = 0.2$$

$$v_{\text{avg}} = v_f + x(v_g - v_f)$$

$$= (0.001036 \text{ m}^3/\text{kg}) + (0.2)((2.3593 - 0.001036) \text{ m}^3/\text{kg})$$
$$= 0.473 \text{ m}^3/\text{kg}$$

$$V = m v = (10 \text{ kg})(0.473 \text{ m}^3/\text{kg}) = 4.73 \text{ m}^3$$

Superheated Vapor

To the right of the saturated vapor line and at T_s above T_{cr} , a substance exists as **superheated vapor**.

Since the superheated region is a **single-phase region** (vapor phase only), T and P are no longer **dependent** properties, and they can conveniently be used as the **2** independent properties in the tables.

	v	u	h
$T, ^\circ\text{C}$	m^3/kg	kJ/kg	kJ/kg
<hr/>			
$P = 0.1 \text{ MPa} (99.61^\circ\text{C})$			
<hr/>			
Sat.	1.6941	2505.6	2675.0
100	1.6959	2506.2	2675.8
150	1.9367	2582.9	2776.6
\vdots	\vdots	\vdots	\vdots
1300	7.2605	4687.2	5413.3
<hr/>			
$P = 0.5 \text{ MPa} (151.83^\circ\text{C})$			
<hr/>			
Sat.	0.37483	2560.7	2748.1
200	0.42503	2643.3	2855.8
250	0.47443	2723.8	2961.0

- ✚ A saturated mixture can be treated as a combination of two subsystems: the saturated liquid and the saturated vapor of unknown masses.
- ✚ Properties are listed against T for selected P starting with the saturated vapor data. T_{sat} is given in parentheses following P value.
- ✚ Compared to saturated vapor, superheated vapor is characterized by:

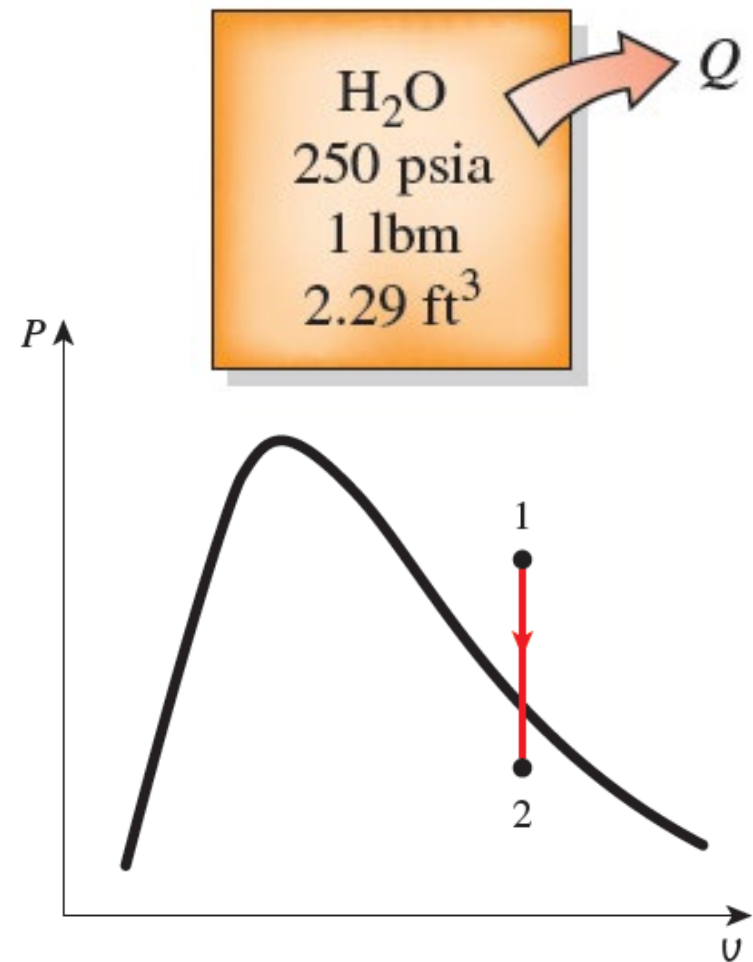
- Lower pressures ($P < P_{\text{sat}}$ at a given T)
- Higher temperatures ($T > T_{\text{sat}}$ at a given P)
- Higher specific volumes ($v > v_g$ at a given P or T)
- Higher internal energies ($u > u_g$ at a given P or T)
- Higher enthalpies ($h > h_g$ at a given P or T)

Example

One pound-mass of water fills a 2.29-ft³ rigid container at an initial pressure of 250 psia. The container is then cooled to 100°F. Determine the initial temperature and final pressure of the water.

Answer

- 1 ft (foot, feet) = 12 inch = 30.48 cm
- 1 lbm (pound) = 453.5924 g
- 1 psia (pound per square inch absolute) = 6894.76 Pa
- 1 Btu (British thermal unit) = 1055.06 J



$$v_1 = \frac{V}{m} = \frac{2.29 \text{ ft}^3}{1 \text{ lbm}} = 2.29 \text{ ft}^3/\text{lbm}$$

TABLE A-5E

Saturated water—Pressure table

Press., P psia	Sat. temp., T_{sat} °F	Specific volume, ft ³ /lbm		Internal energy, Btu/lbm			Enthalpy, Btu/lbm			Entropy, Btu/lbm·R		
		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
190	377.52	0.01833	2.4040	350.24	763.31	1113.6	350.89	847.19	1198.1	0.53839	1.01191	1.5503
200	381.80	0.01839	2.2882	354.78	759.32	1114.1	355.46	843.33	1198.8	0.54379	1.00219	1.5460
250	400.97	0.01865	1.8440	375.23	741.02	1116.3	376.09	825.47	1201.6	0.56784	0.95912	1.5270
300	417.35	0.01890	1.5435	392.89	724.77	1117.7	393.94	809.41	1203.3	0.58818	0.92289	1.5111
350	431.74	0.01912	1.3263	408.55	709.98	1118.5	409.79	794.65	1204.4	0.60590	0.89143	1.4973

At 250 psia, $v_g = 1.8440 \text{ ft}^3/\text{lbm}$.

Since $v_1 > v_g$, the water is initially in the superheated vapor region. The temperature is determined to be:

$$\left. \begin{array}{l} P_1 = 250 \text{ psia} \\ v_1 = 2.29 \text{ ft}^3/\text{lbm} \end{array} \right\} T_1 = 550^\circ\text{F}$$

TABLE A-6ESuperheated water (*Concluded*)

T °F	v ft ³ /lbm	u Btu/lbm	h Btu/lbm	s Btu/lbm·R
$P = 250$ psia (400.97°F)				
Sat.	1.8440	1116.3	1201.6	1.5270
450	2.0027	1141.3	1234.0	1.5636
500	2.1506	1164.1	1263.6	1.5953
550	2.2910	1185.6	1291.5	1.6237
600	2.4264	1206.3	1318.6	1.6499
650	2.5586	1226.8	1345.1	1.6743

✚ This is a constant volume cooling process ($v = V/m = \text{constant}$).

✚ The final state is **saturated mixture** and thus the pressure is the **saturation pressure** at the final T:

TABLE A-4E

Saturated water—Temperature table

Temp., T °F	Sat. press., P_{sat} psia	Specific volume, ft ³ /lbm		Internal energy, Btu/lbm			Enthalpy, Btu/lbm			Entropy, Btu/lbm-R		
		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
95	0.81643	0.01612	403.74	63.04	978.52	1041.6	63.04	1039.5	1102.6	0.12065	1.87408	1.9947
100	0.95052	0.01613	349.83	68.03	975.14	1043.2	68.03	1036.7	1104.7	0.12961	1.85225	1.9819
110	1.2767	0.01617	264.96	78.01	968.36	1046.4	78.02	1031.0	1109.0	0.14728	1.80970	1.9570

$$\left. \begin{aligned} T_2 &= 100^\circ\text{F} \\ v_2 &= v_1 = 2.29 \text{ ft}^3/\text{lbm} \end{aligned} \right\} \begin{aligned} P_2 &= P_{\text{sat}} @ 100^\circ\text{F} \\ &= 0.9505 \text{ psia} \end{aligned}$$

When a substance undergoes a process in a closed rigid tank, **v** remains **constant**, and the process appears as a **vertical line** in the **P-v diagram**.

Compressed Liquid

- ✚ **Compressed liquid** tables are not as commonly available, due to the relative independence of compressed liquid properties from pressure.
- ✚ Variation of properties of **compressed liquid** with pressure is very mild. Increasing the pressure **100 times** often causes properties to change less than **1 %**.
- ✚ In the absence of **compressed liquid** data, a general approximation is to *treat compressed liquid as saturated liquid at the given temperature*.
- ✚ **Compressed liquid** properties depend on **T** much more strongly than they do on **P**.

$$y \cong y_f @ T$$

$$y = v, u \text{ or } h$$

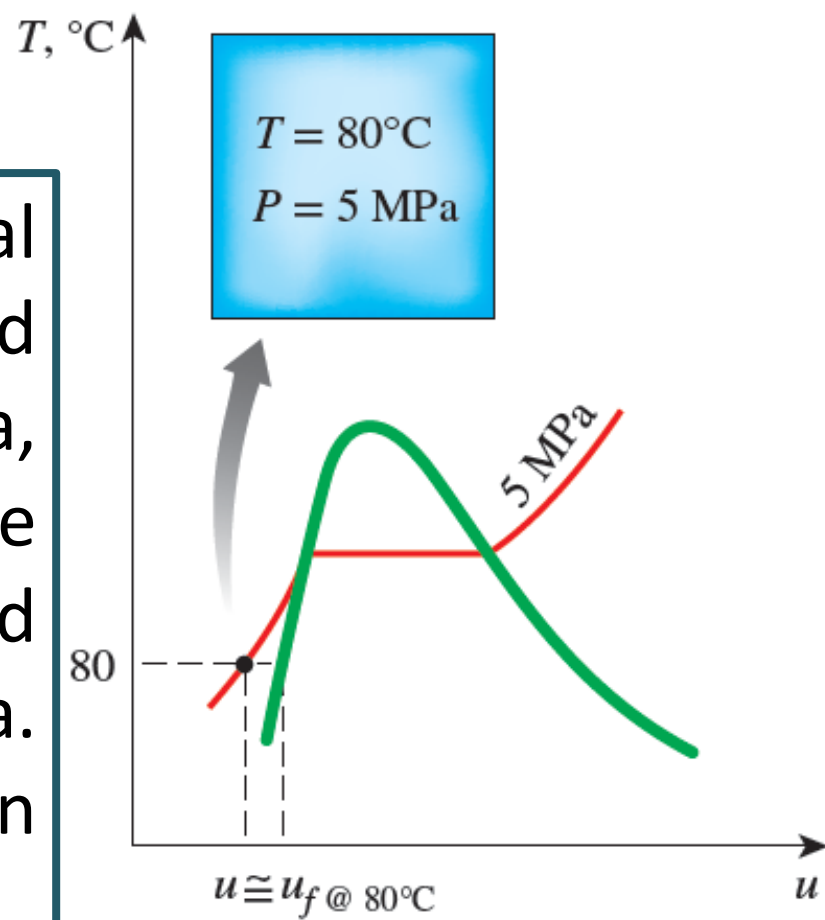
- # The property whose value is most sensitive to variations in P is the enthalpy h .
- # Although the preceding approximation results in negligible error in v and u , the error in h may reach undesirable levels, particularly at high T and P .
- # In general, a compressed liquid is characterized by:

- Higher pressures ($P > P_{\text{sat}}$ at a given T)
- Lower temperatures ($T < T_{\text{sat}}$ at a given P)
- Lower specific volumes ($v < v_f$ at a given P or T)
- Lower internal energies ($u < u_f$ at a given P or T)
- Lower enthalpies ($h < h_f$ at a given P or T)

Unlike superheated vapor, the compressed liquid properties are not much different from the corresponding saturated liquid values.

Example

Determine the internal energy of compressed liquid water at 80°C and 5 MPa , using (a) data from the compressed liquid table and (b) saturated liquid data. What is the error involved in the second case?



Answer

- At 80°C , $P_{\text{sat}} = 47.416\text{ kPa}$ ($< 5\text{ MPa}$). We obviously have compressed liquid.
- From the **compressed** liquid table:

$$\left. \begin{array}{l} P = 5 \text{ MPa} \\ T = 80^\circ\text{C} \end{array} \right\} u = 333.82 \text{ kJ/kg}$$

- From the **saturation** table:

$$u \cong 334.97 \text{ kJ/kg}$$

- **Error involved:**

$$\frac{334.97 - 333.82}{333.82} \times 100 = 0.34\%, \quad (< 1\%)$$

Reference State and Reference Values

- ✚ The values of u , h , and s cannot be measured directly, and they are **calculated** from measurable properties using the relations between thermodynamic properties.
- ✚ However, those relations give the **changes** in properties, **not the values** of properties at specified states. Therefore, we need to choose a convenient *reference state* and assign a value of **zero** for a convenient property or properties at that state.
- ✚ For water, the state of saturated liquid at **0.01°C** is taken as the reference state, and the **internal energy** and **entropy** are assigned **zero** values at that state.
- ✚ For refrigerant-134a, the state of saturated liquid at **-40°C** is taken as the reference state, and the **enthalpy** and **entropy** are assigned **zero** values at that state.