ESO201A : THERMODYNAMICS
2021-22 Ist semester
IIT Kanpur

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Lecture 4

Changes in internal energy:

As engineers, we are concerned with processes involving changes of temperature, pressure, phase, and composition.

Steam boiler

Changes of phase from water to steam

Changes in composition due to burning of fuel (usually coal)

Air compressor

Changes in Temperature and Pressure

Changes in internal energy:

The energy transfer in the form of heat and work in all such processes results in changes of internal energy U. Hence it is important to have a better understanding of changes in U.

At a microscopic level, changes in U are due to changes of average kinetic and potential energies of constituent atoms and molecules

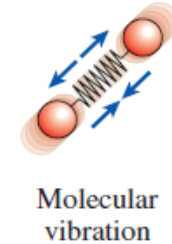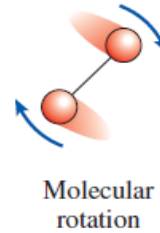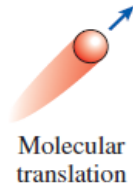$$\Delta U = \Delta \langle k.e. \rangle + \Delta \langle p.e. \rangle$$

$\Delta \langle k.e. \rangle$ = Change in average kinetic energy of atoms and molecules

$\Delta \langle p.e. \rangle$ = Change in average potential energy of atoms and molecules

$\boxed{\Delta \langle \text{k.e.} \rangle}$ (translational k.e. + rotational k.e. + vibrational k.e.)

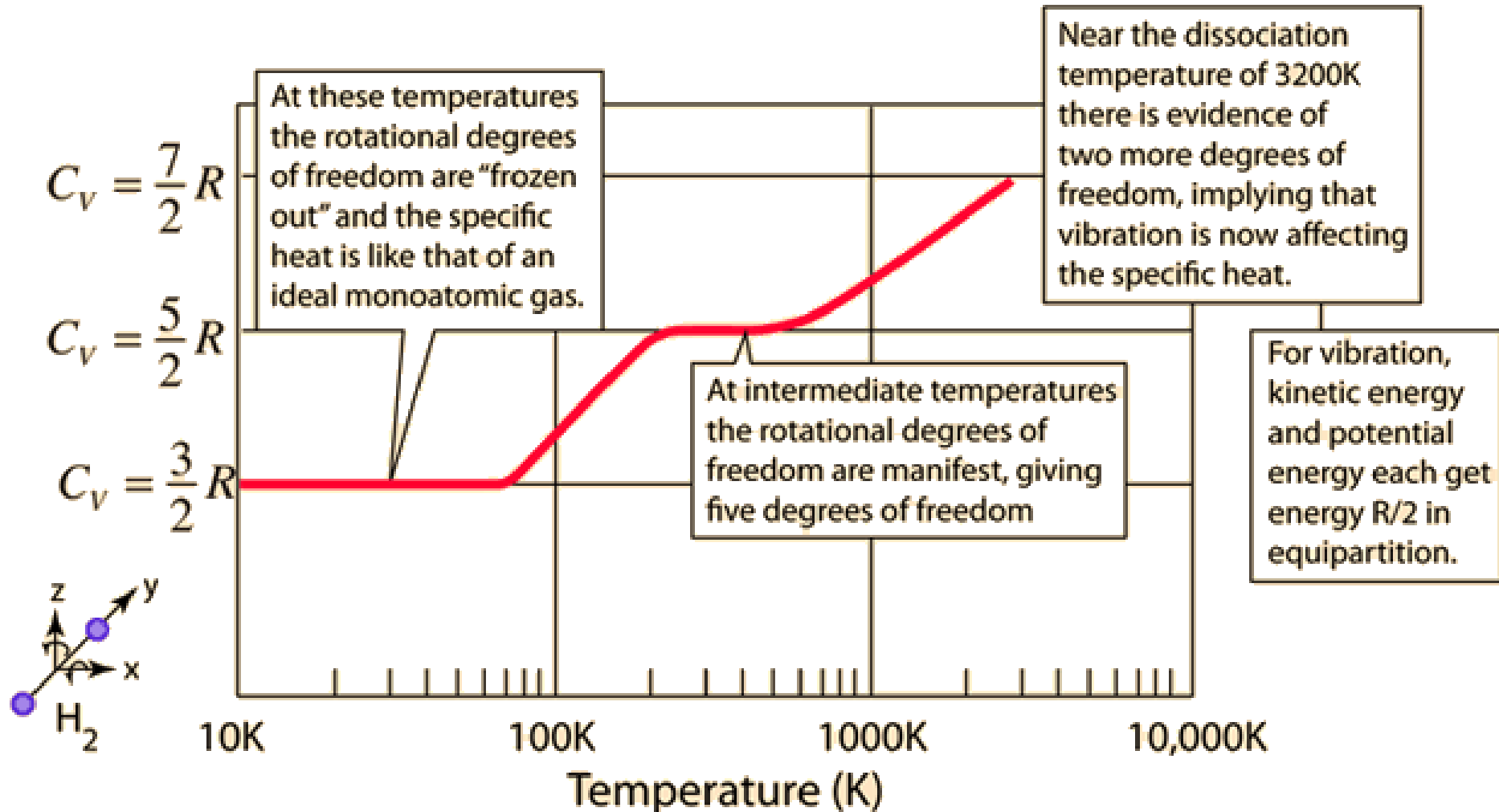Molecular translation   Molecular rotation   Molecular vibration

Processes involving changes of temperature are affected by changes In kinetic energies due to translation, rotation, and (intra-molecular) vibration of molecules

The amount of heat per kg or per mole of a substance required to increase the temperature by 1 ^{0}C is known as specific heat .

So, these microscopic kinetic energies directly affect specific heat.

Specific heat at constant volume (Cv) refer to amount of heat absorbed per unit mass or per mole to increase temperature by 1 ^{0}C at constant volume. Similarly specific heat at constant pressure (CP) is defined.   Ref. : Cengel and Boles , 8th Edition (2015)

Hydrogen gas is composed of diatomic molecules of H_2. The following plot shows how specific heat at constant volume (Cv) is affected by kinetic energies due to translation, rotation, and vibration of H_2 molecules

Near the dissociation temperature of 3200K there is evidence of two more degrees of freedom, implying that vibration is now affecting the specific heat.

At these temperatures the rotational degrees of freedom are "frozen out" and the specific heat is like that of an ideal monoatomic gas.

$$C_v = \frac{7}{2}R$$

$$C_v = \frac{5}{2}R$$

$$C_v = \frac{3}{2}R$$

At intermediate temperatures the rotational degrees of freedom are manifest, giving five degrees of freedom

For vibration, kinetic energy and potential energy each get energy R/2 in equipartition.

H_2

10K   100K   1000K   10,000K

Temperature (K)

$$\boxed{\Delta \langle \text{p.e.} \rangle} \quad (\text{Intermolecular p.e. } + \text{ Intramolecular p.e.})$$

Intermolecular p. e. Due to binding forces between the molecules.   These are important in changes in which average distance between the molecules change, e.g., change in T (fluids, solids), P (for gases), and phase (e.g. liquid→vapor, solid→liquid) and changes of composition without a chemical reaction (dissolution). These binding forces include

(i)   Van der Waal's forces : These are the non-ionic forces between the molecules

(ii) Ionic forces : due to charge-charge interactions. For example, common salt (NaCl) has a large melting point (801 ^{0}C) due to strong ionic forces between Na$^+$ and Cl$^-$ ions.

Intermolecular p. e. directly affect physical properties. For example :

CH_4 (Methane) is a gas at ambient conditions because intermolecular forces are weakly attractive due to non-ionic nature of interactions

In CH_3-OH (Methanol), due to strong electronegativity of oxygen in –OH group, it attracts electron cloud towards itself. As a result, H atom of –OH group develops a slightly positive charge and O atom of –OH group develops a slightly negative charge.   This leads to strong hydrogen bonded (ionic) interactions between different molecules.   As a result of these strong interactions, methanol exists in a liquid state at ambient conditions.

Intermolecular p. e.   These binding forces are important during heating/cooling of a material, compression/expansion of a gas, phase changes, dissolution, and mixing processes

Solid   Liquid   Gas

Increase in Intermolecular potential energy
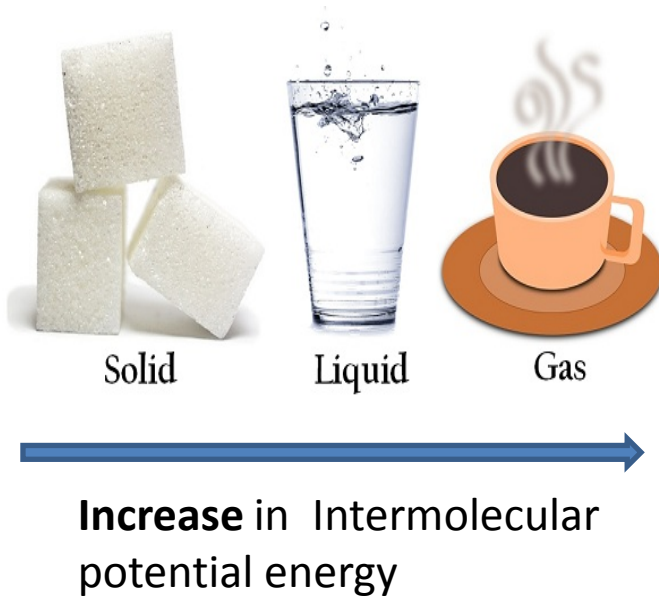
Dissolution of sugar in water

<u>Intramolecular p. e.</u>   These binding forces are important during changes of composition (e.g., reactions)

1.Combustion

2.Reforming of methane
(used in Ammonia production)

Table 1: Basic processes for syngas production from methane.

Process	Reaction	H_2/CO ratio	$\Delta H_{1173\,K}$ [kJ mol^{-1}]
Steam reforming	$CH_4 + H_2O \rightarrow CO + 3\,H_2$	3:1	225.7
CO$_2$ reforming (dry reforming)	$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2$	1:1	258.8
Oxy reforming (partial oxidation)	$CH_4 + 1/2\,O_2 \rightarrow CO + 2\,H_2$	2:1	−23.1

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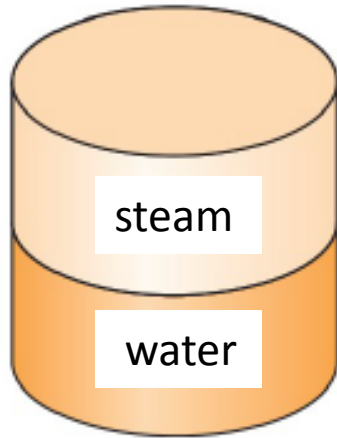
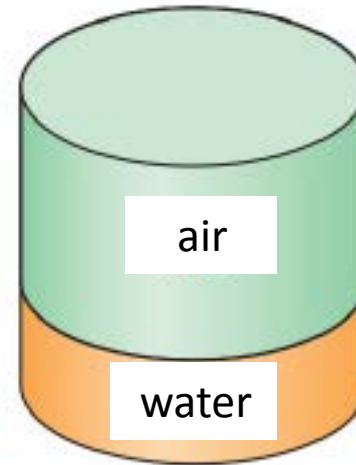A pure substance need not contain a single element or a single compound.

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

Air

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

Analysis of processes involving **pure** substance:
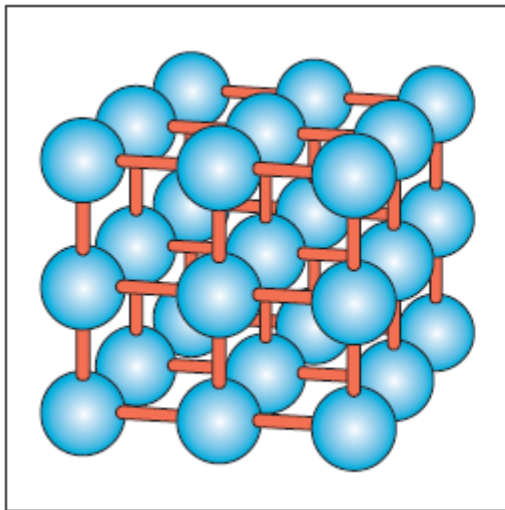

(water + steam) is a pure substance

(water + air) is NOT a pure substance
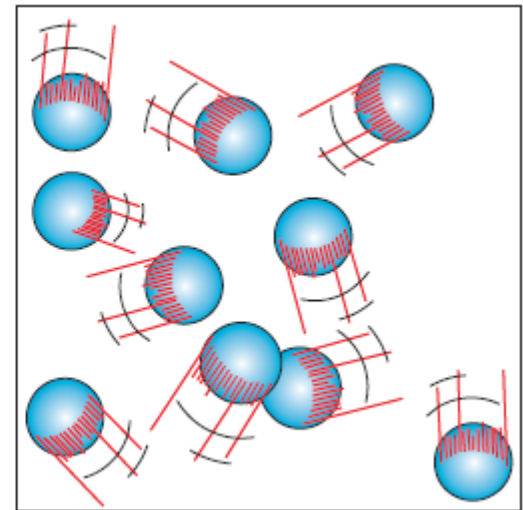
A pure substance can exist in different phases

SOLID
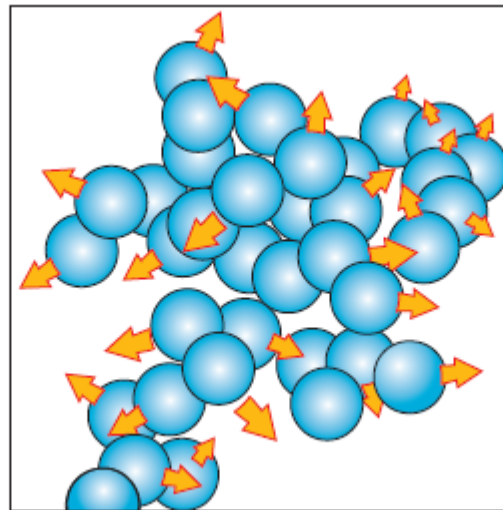
LIQUID

GAS

State postulate :
(for a single phase of a pure substance)

It is known experimentally that whenever temperature and pressure of a single phase of a pure substance (e.g., liquid water or air) are specified, all other intensive properties of water have unique values.

For example, water at T = 50 ^{0}C and P = 1 atm has a density of 988 kg/m^3 and a viscocity of 0.5474 x 10^{-3} Ns/m^2.

Thus, θ = f (T, P) where θ = density, viscosity, refractive index, specific heat or any other intensive property [Recall that mathematically if z = f(x,y), then z has a unique value for given values of x and y]

Similarly, temperature (T) and specific volume (v) of water can determine all other intensive properties uniquely, i.e., θ = f (T, v).

The above experimental observations are formally stated as a **state postulate :**

In processes not involving electrical, magnetic , stress-strain or surface tension effects, the state of a given phase of a pure substance is uniquely determined by specifying two independent, intensive properties.

Throughout this course, we will consider that THERE ARE NO ELECTRIC, MAGNETIC, STRESS-STRAIN, AND SURFACE TENSION EFFECTS, unless stated explicitly.
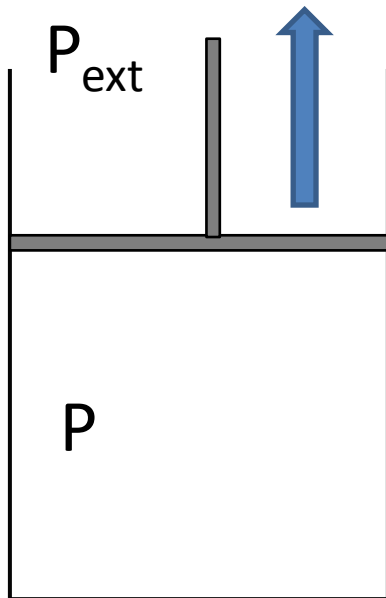
Expansion of a pure substance :

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

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

where,

$$W_{out} = \int_{1}^{2} P_{ext}\, dV$$

For an expansion process, $P > P_{ext}$
Therefore, one can write
$(P - \Delta P) = P_{ext}$

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, $\Delta P \to 0$. Hence third term on the right hand side of above equation can be <u>neglected</u> 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 <u>sufficiently slow</u> and <u>pressure is constant</u> 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

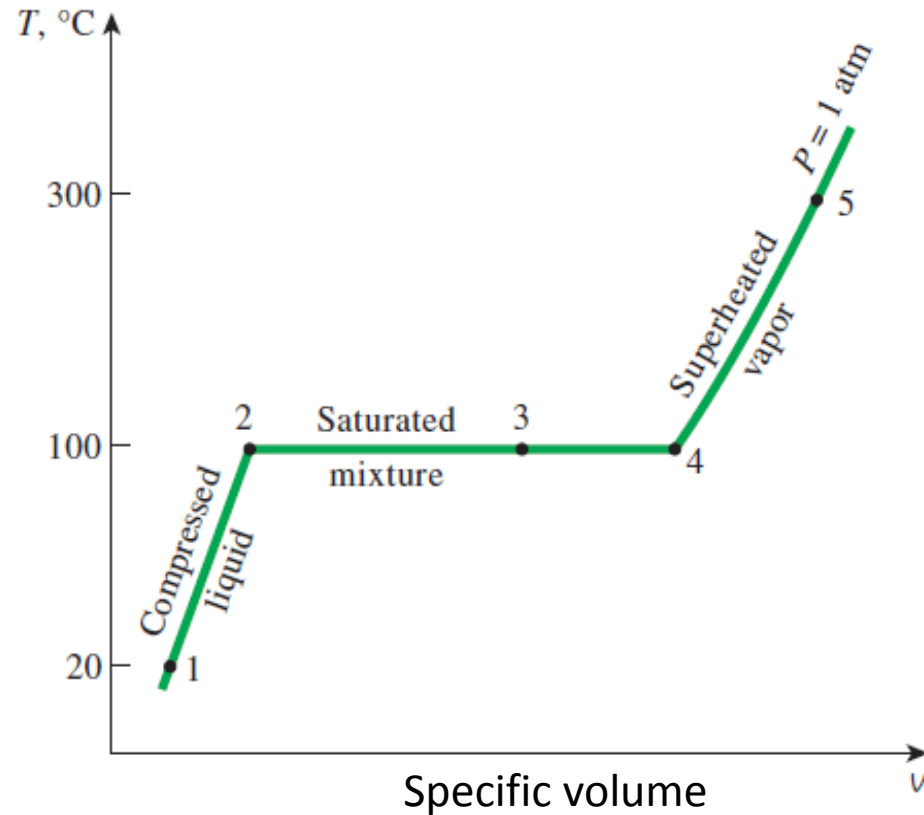# Constant pressure expansion of a pure substance :

The above 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 atm (101.325 N/m2)

Ref. : Cengel and Boles , 8th Edition (2015)
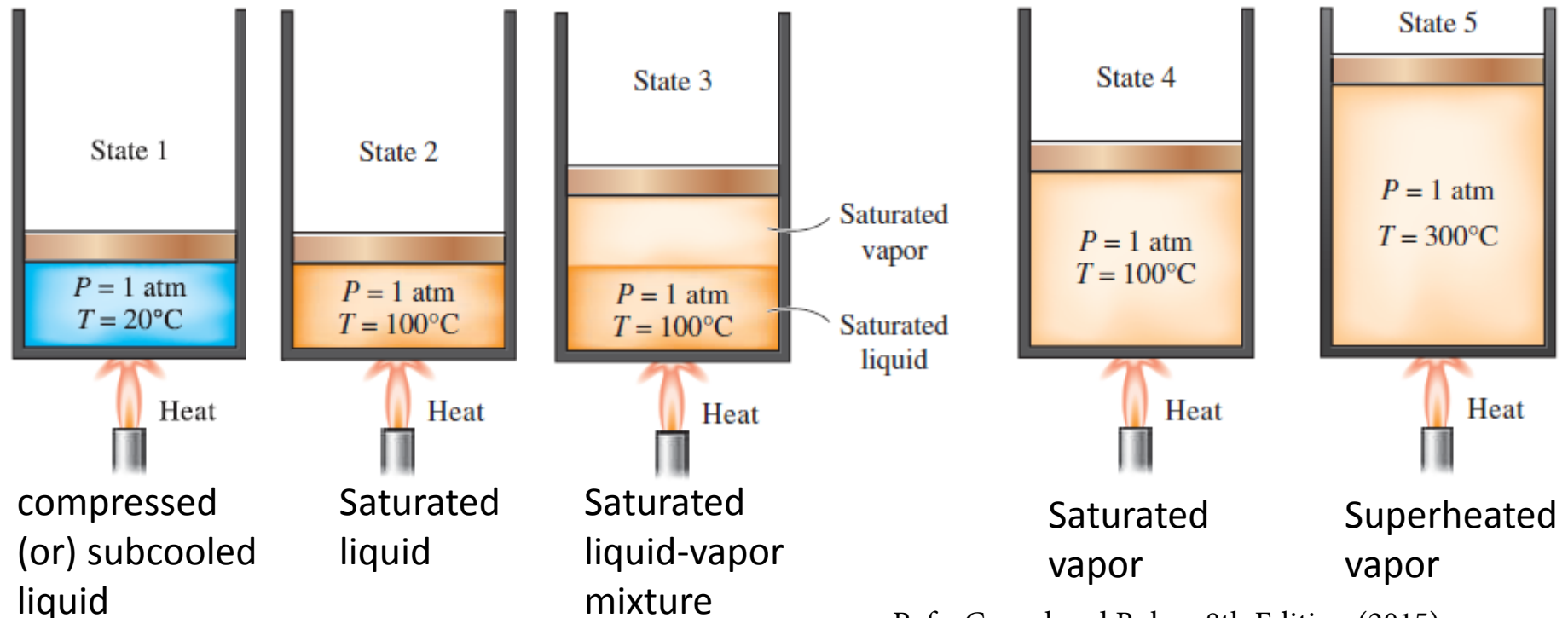
Constant pressure expansion of water at 1 atm :

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.

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

Constant pressure expansion of water at 1 atm :

According to the derivation in previous slides, for a constant pressure expansion process from 1→2 (see diagram on last slide)

Q_{in} (1→2) = $H_2 - H_1$

　　　　 = $m (h_2 - h_1)$

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 at 1 atm :

For the process from 2→4 (see previous slides)

Q_{in} (2→4) = $H_4 - H_2$

$\qquad\qquad$ = $m (h_4 - h_2)$

$\qquad\qquad$ = $m (h_{g@1atm} - h_{f@1atm})$

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 tables known as "steam tables".

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_{sat} = 100 ^{0}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_{sat} = f(P).

Press., P kPa	Sat. temp., T_{sat} °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

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