$$\langle P.E.\rangle = \langle Intermolecular\ P.E. + Intramolecular\ P.E. + Intra\ atomic\ P.E.\rangle$$

<u>Intermolecular P. E.</u> 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) 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.

<u>Intermolecular P. E.</u> 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.
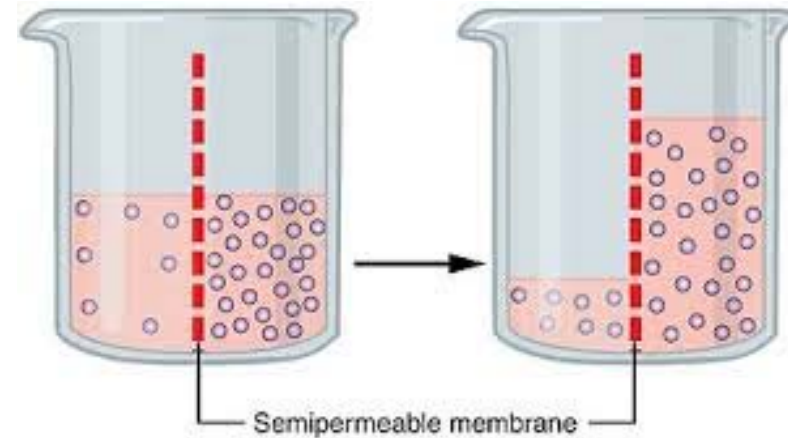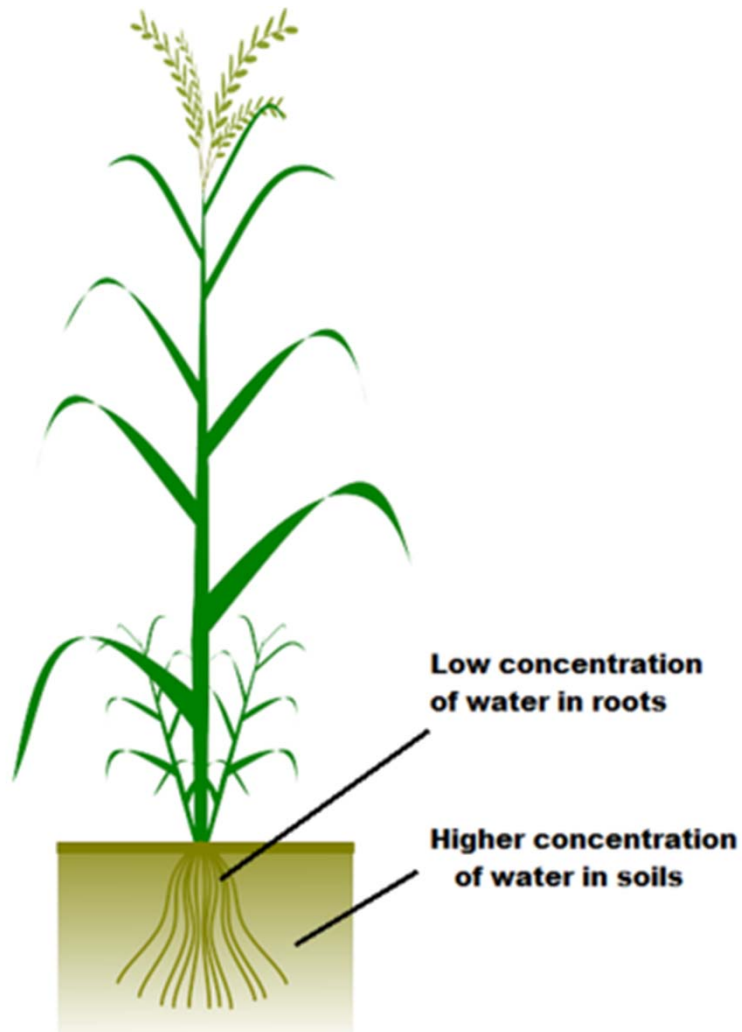
Intermolecular P. E.   These binding forces are important during heating/cooling of a material, compression/expansion of a gas, phase changes, dissolution, mixing,
And separation processes

Solid   Liquid   Gas

Increase in Intermolecular potential energy
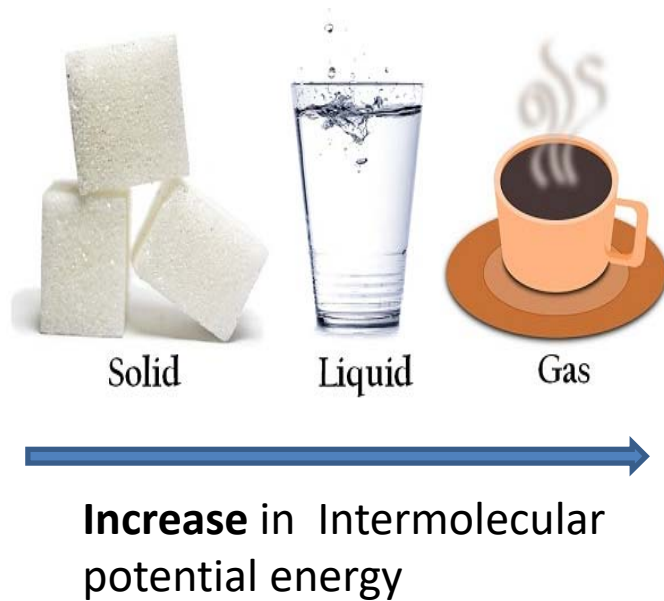
Dissolution of sugar in water

Intermolecular P. E.   These binding forces are important during changes of composition

Osmosis

Semipermeable membrane

Low concentration of water in roots

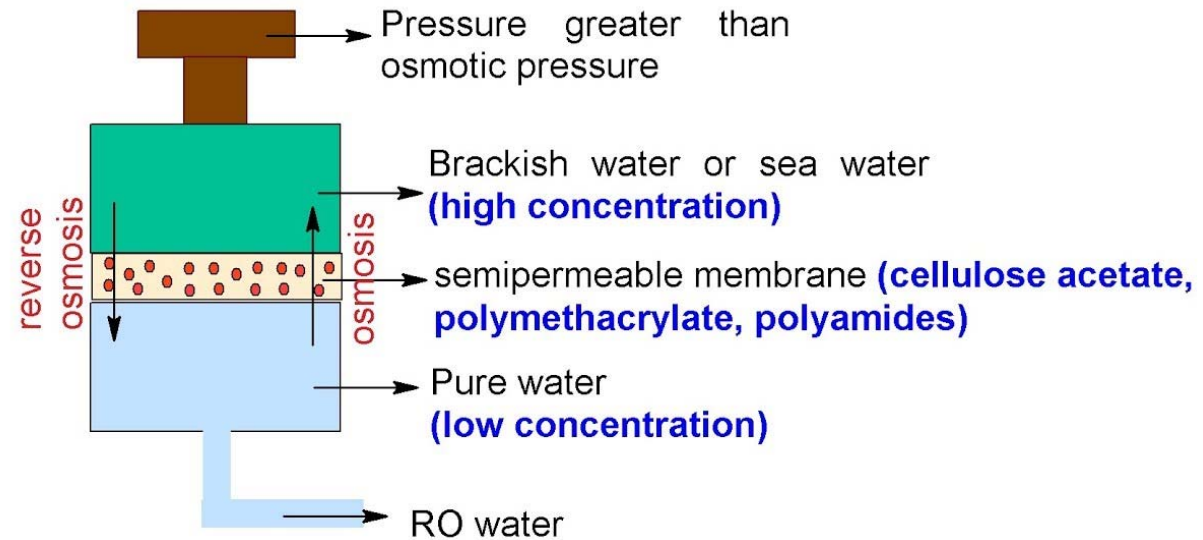Higher concentration of water in soils

Osmosis process is used by plant to absorb water form the soil

Intermolecular P. E.   These binding forces are important during changes of composition

Reverse Osmosis

REVERSE OSMOSIS PROCESS

Pressure greater than osmotic pressure

Brackish water or sea water **(high concentration)**

semipermeable membrane **(cellulose acetate, polymethacrylate, polyamides)**

Pure water **(low concentration)**

RO water

reverse osmosis

osmosis

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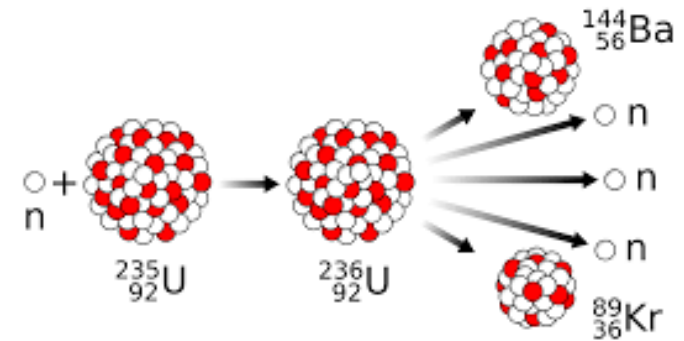
1.Combustion

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

Intra atomic P. E.   These binding forces are important during nuclear fission reactions

Steel pressure vessel

Steam

Fuel elements

Water

Control rods

Pump

$^0_1n +$ $^{235}_{92}U$ → $^{236}_{92}U$ → $^{144}_{56}Ba$
n
n
n
$^{89}_{36}Kr$
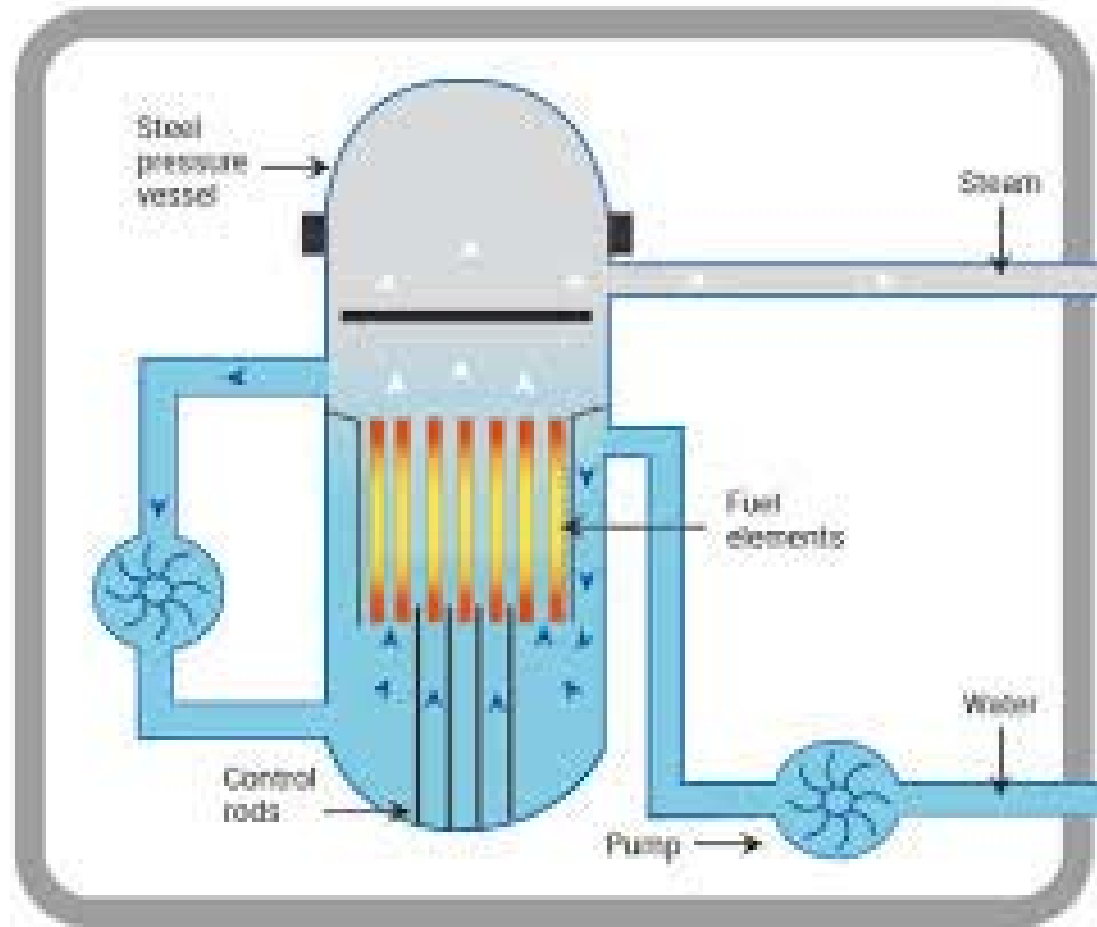
Properties of compressed liquid:

As per the state postulate, the state of compressed liquid is completely determined by specifying temperature (T) and pressure (P). For a compressed liquid, $P > P_{sat}$ 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

$$u_{f@T} = u(T,P_{sat})$$
$$v_{f@T} = v(T,P_{sat})$$
$$s_{f@T} = s(T,P_{sat})$$

Properties of compressed liquid:

The specific enthalpy of a compressed liquid is estimated as :

$$h(T,P) - h(T,P_{sat}) = \int_{Psat}^{P} \left(\frac{\partial h}{\partial P} \right)_T dP$$

$$= \int_{Psat}^{P} \left(\frac{\partial (u + Pv)}{\partial P} \right)_T dP$$

$$\approx v_{f@Psat}(P - P_{sat})$$

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

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

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

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

Example: Determine the enthalpy of compressed liquid water at 80 ^{0}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

TABLE A–7

Compressed liquid water

T	v	u	h	s	v	u	h	s	v	u	h	s
°C	m³/kg	kJ/kg	kJ/kg	kJ/kg·K	m³/kg	kJ/kg	kJ/kg	kJ/kg·K	m³/kg	kJ/kg	kJ/kg	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

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

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, m³/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

Determine the missing properties and the phase descriptions in the following table for water:

	T, °C	P, kPa	u, kJ/kg	X	Phase description
(a)		200		0.6	
(b)	125		1600		
(c)		1000	2950		
(d)	75	500			
(e)		850		0.0	

Press., P kPa	Sat. temp., T_{sat} °C	Specific volume, m³/kg		Internal energy, kJ/kg		
		Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g
200	120.21	0.001061	0.88578	504.50	2024.6	2529.1

$$T = T_{sat@200kPa} = \mathbf{120.21^0C}$$

$$u = x\,u_{\,g} + (1 - x)\,u_{\,f}$$

$$u = u_{\,f} + x\,u_{\,fg}$$

$$u = 504.5 + (0.6)2024.6$$

$$\underline{u = 1719.6 \text{ kJ/kg}}$$

Determine the missing properties and the phase descriptions in the following table for water:

	T, °C	P, kPa	u, kJ/kg	x	Phase description
(a)		200		0.6	
(b)	125		1600		
(c)		1000	2950		
(d)	75	500			
(e)		850		0.0	

		Specific volume, m³/kg		Internal energy, kJ/kg		
Temp., T°C	Sat. press., P_{sat} kPa	Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g
125	232.23	0.001065	0.77012	524.83	2009.5	2534.3

$$P = P_{sat@125\,C} = 232.23 \text{ kPa}$$

$$X = \frac{u - u_f}{u_{fg}}$$

$$X = \frac{1600 - 524.83}{2009.5}$$

$$\underline{x = 0.535}$$

Determine the missing properties and the phase descriptions in the following table for water:

	T, °C	P, kPa	u, kJ/kg	x	Phase description
(a)		200		0.6	
(b)	125		1600		
(c)		1000	2950		
(d)	75	500			
(e)		850		0.0	

		Specific volume, m³/kg		Internal energy, kJ/kg		
Press., P kPa	Sat. temp., T_{sat} °C	Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g
1000	179.88	0.001127	0.19436	761.39	1821.4	2582.8

$$u = 2950 \text{ kJ/kg} > u_g \quad \text{at P} = 1000 \text{ kPa}$$

Determine the missing properties and the phase descriptions in the following table for water:

	T, °C	P, kPa	u, kJ/kg	x	Phase description
(a)		200		0.6	
(b)	125		1600		
(c)		1000	2950		
(d)	75	500			
(e)		850		0.0	

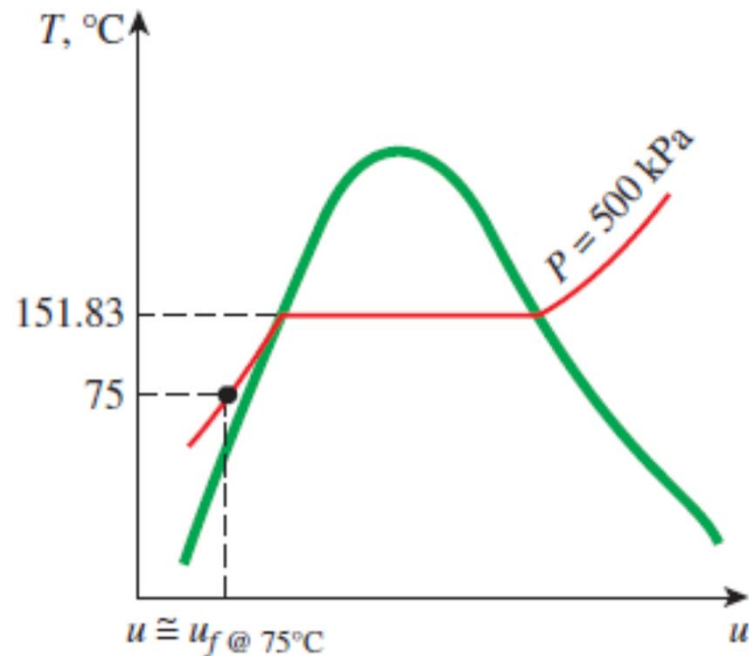| T	v	u	h	s
°C	m³/kg	kJ/kg	kJ/kg	kJ/kg·K
	P = 1.00 MPa (179.88°C)			
350	0.28250	2875.7	3158.2	7.3029
400	0.30661	2957.9	3264.5	7.4670

Linear interpolation yields

$$\frac{2957.9 - 2950}{2957.9 - 2875.7} = \frac{400 - T}{400 - 350}$$

Upon solving, we get   T = 395.2°C

Determine the missing properties and the phase descriptions in the following table for water:

	T, °C	P, kPa	u, kJ/kg	X	Phase description
(a)		200		0.6	
(b)	125		1600		
(c)		1000	2950		
(d)	75	500			
(e)		850		0.0	

$T = 75^0C < T_{sat}$@500 kPa

It's a compressed liquid or subcooled liquid state

Since liquid properties are not affected greatly by pressure, we can do the following approximation :

$$u \cong u_f @ 75^0C$$

Determine the missing properties and the phase descriptions in the following table for water:

	T, °C	P, kPa	u, kJ/kg	x	Phase description
(a)		200		0.6	
(b)	125		1600		
(c)		1000	2950		
(d)	75	500			
(e)		850		0.0	

		Specific volume, m³/kg			Internal energy, kJ/kg		
Temp., T °C	Sat. press., P_{sat} kPa	Sat. liquid, v_f	Sat. vapor, v_g		Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g
75	38.597	0.001026	4.1291		313.99	2161.3	2475.3

$$u \cong u_f @ 75^0C = 313.99 \text{ kJ/kg}$$

Determine the missing properties and the phase descriptions in the following table for water:

	T, °C	P, kPa	u, kJ/kg	x	Phase description
(a)		200		0.6	
(b)	125		1600		
(c)		1000	2950		
(d)	75	500			
(e)		850		0.0	

|		Specific volume, m³/kg			Internal energy, kJ/kg		
Press., P kPa	Sat. temp., T_{sat} °C	Sat. liquid, v_f	Sat. vapor, v_g		Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g
850	172.94	0.001118	0.22690		731.00	1846.9	2577.9

$$T = T_{sat} @ 850kPa = 172.94^0C$$

$$u = u_f @ 850kPa = 731.00 \text{ kJ/kg}$$

Relative Humidity :

The relative humidity is the percentage of water in air relative to the maximum amount air can hold at a given temperature

$$P_{atm} = P_a + P_v$$

Air
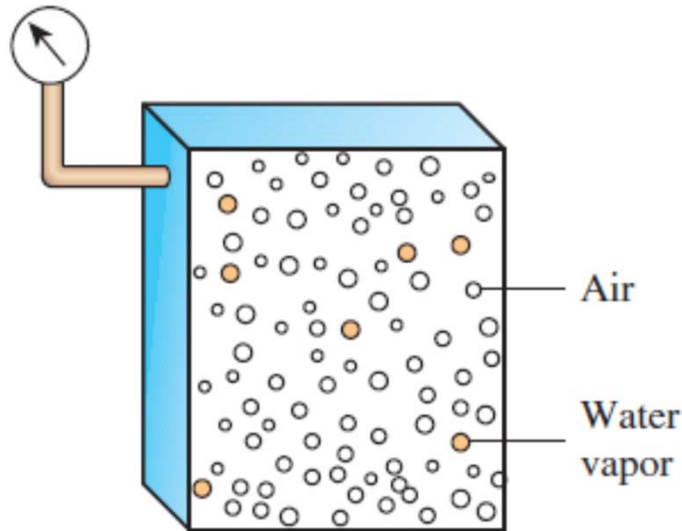
Water vapor

Humidity affects thermal comfort as well as many processes occurring in the environment including drying

$$P_{atm} = P_a + P_v$$
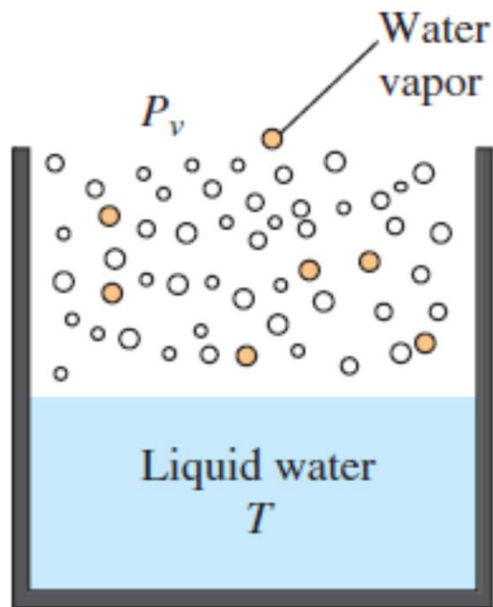
Here,

P_{atm} = total pressure of atmosphere

P_a = pressure of dry air

P_v = pressure of water vapor
        in the atmosphere

Relative Humidity :

In order to understand the concept of relative humidity, you need to understand the phase equilibrium between air and water as shown in the figure

Air is in equilibrium with water vapor when
(i)   Temperature and pressure of both air and water are equal
(ii)   pressure of water vapor in air equals the saturation pressure

$$P_v = P_{sat}@T$$

If $P_v > P_{sat}@T$ then water vapor will condense until the pressure of water vapor in air becomes equal to the saturation pressure.

Thus maximum water vapor pressure in air is equal to saturation pressure at the temperature of air.

Relative Humidity :

Thus relative humidity of air (in percentage) is defined as

$$\phi = \left(\frac{P_v}{P_{sat}@T}\right) \times 100$$

For dry air, $\phi = 0$

For saturated air, $\phi = 100 \%$

If air is at 25^0C with a relative humidity of $\phi = 60\%$, then what is the vapor pressure of water in air ?

$$P_{sat}@25^0C = 3.17 \text{ kPa}$$

$$P_v = \left(\frac{\phi}{100}\right) P_{sat}@T$$

$$P_v = \left(\frac{60}{100}\right) 3.17 = 1.9 \text{ kPa}$$

Consequences of humid atmosphere :

What happens when relative humidity φ is close to 100% ?

During summer, we experience a lot of sweating and discomfort.
Coolers do not lead to effective cooling.

During summer, large relative humidity also increases the chance
for precipitation (rain).

During winters, it leads to formation of fog and dew drops.