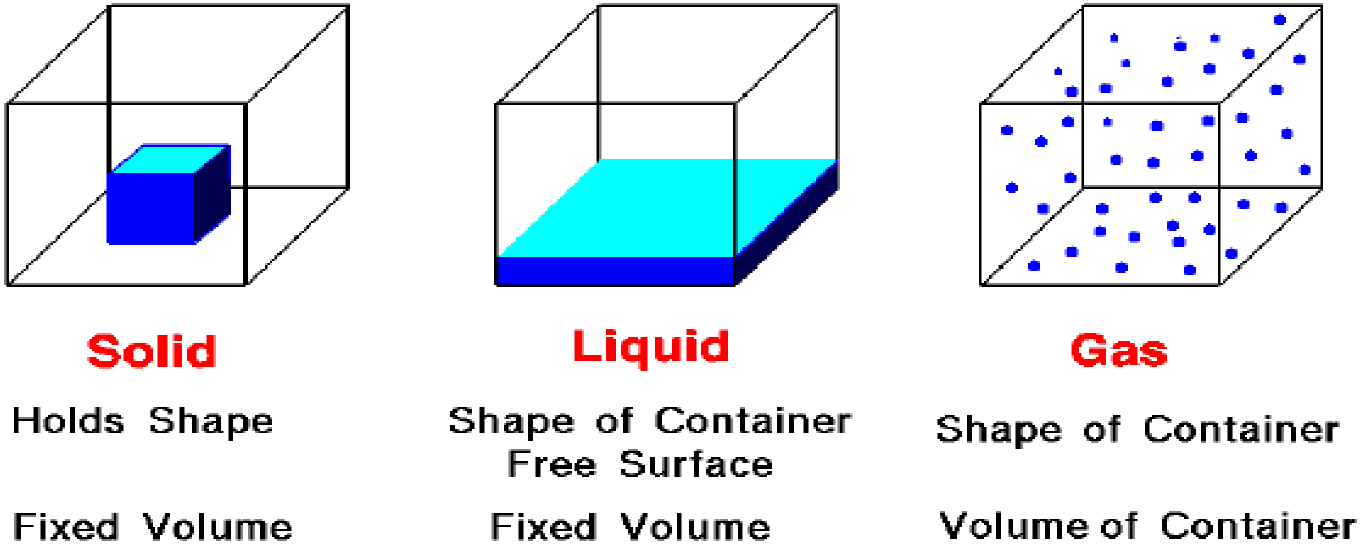
Lecture 2

Properties of Pure Substances

Phases of a Pure Substance:

Macroscopic Level:

3 States of Matter

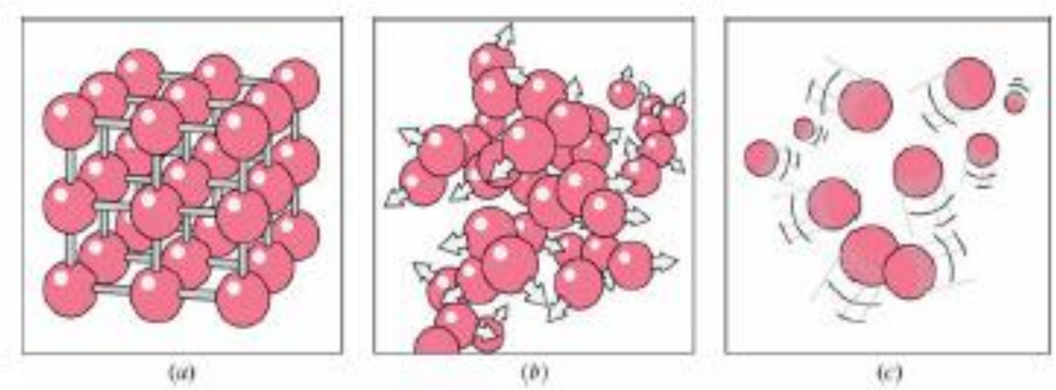


Macroscopic Level:

a) ***Solid:*** Intermolecular bonds are the strongest. The molecules are arranged in a 3-dimensional pattern (lattice), which is repeated throughout.

b) ***Liquid:*** Molecules are no longer at fixed positions and they can translate freely.

c) ***Gas*****:** Intermolecular bonds are the weakest. There is no molecular order and molecules move about at random**.**



Phase Change:

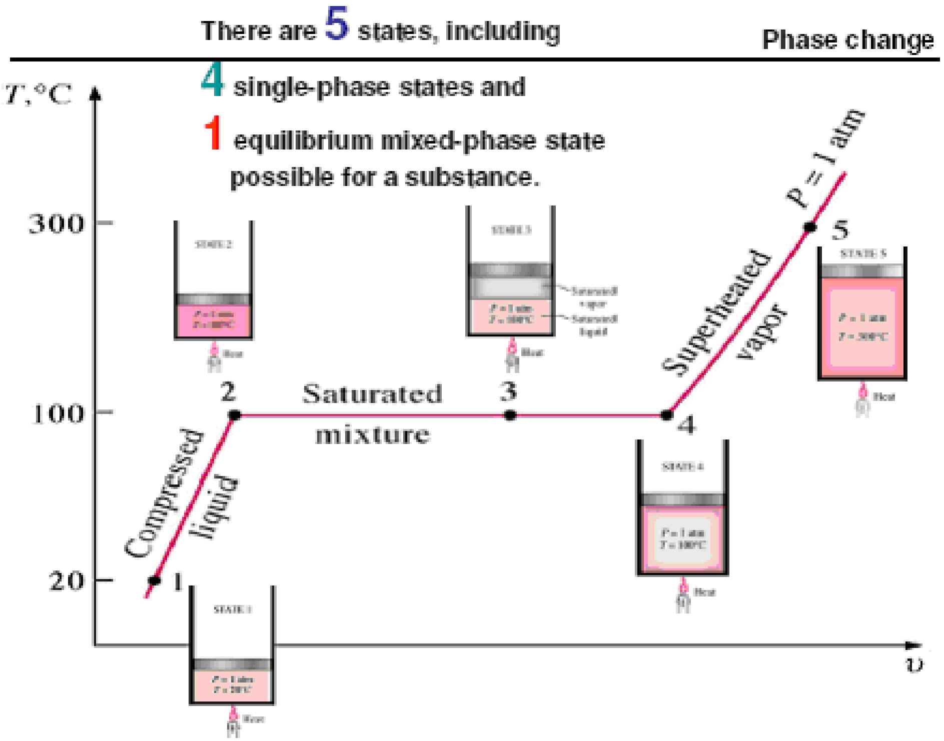
1- Compressed or sub-cooled liquid: The liquid is not about to vaporize.

2- Saturated liquid: The liquid is about to vaporize.

3- Saturated liquid and vapor: There is a mixture**.**

4- Saturated vapor: The vapor is about to condense

5- Superheated vapor: the vapor is not about to condense.



Saturation Temperature and Pressure:

Note:- The temperature at which a liquid starts boiling depends on the pressure and vice versa.

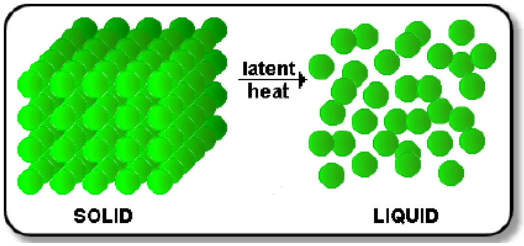
- ✓ At a give pressure, the temperature at which a pure substance changes phase is called the ***saturation temperature.***
- ✓ At a given temperature, the pressure at which a pure substance changes phase is called the ***saturation pressure.***

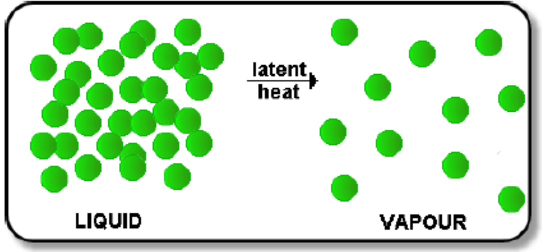
Latent heat:

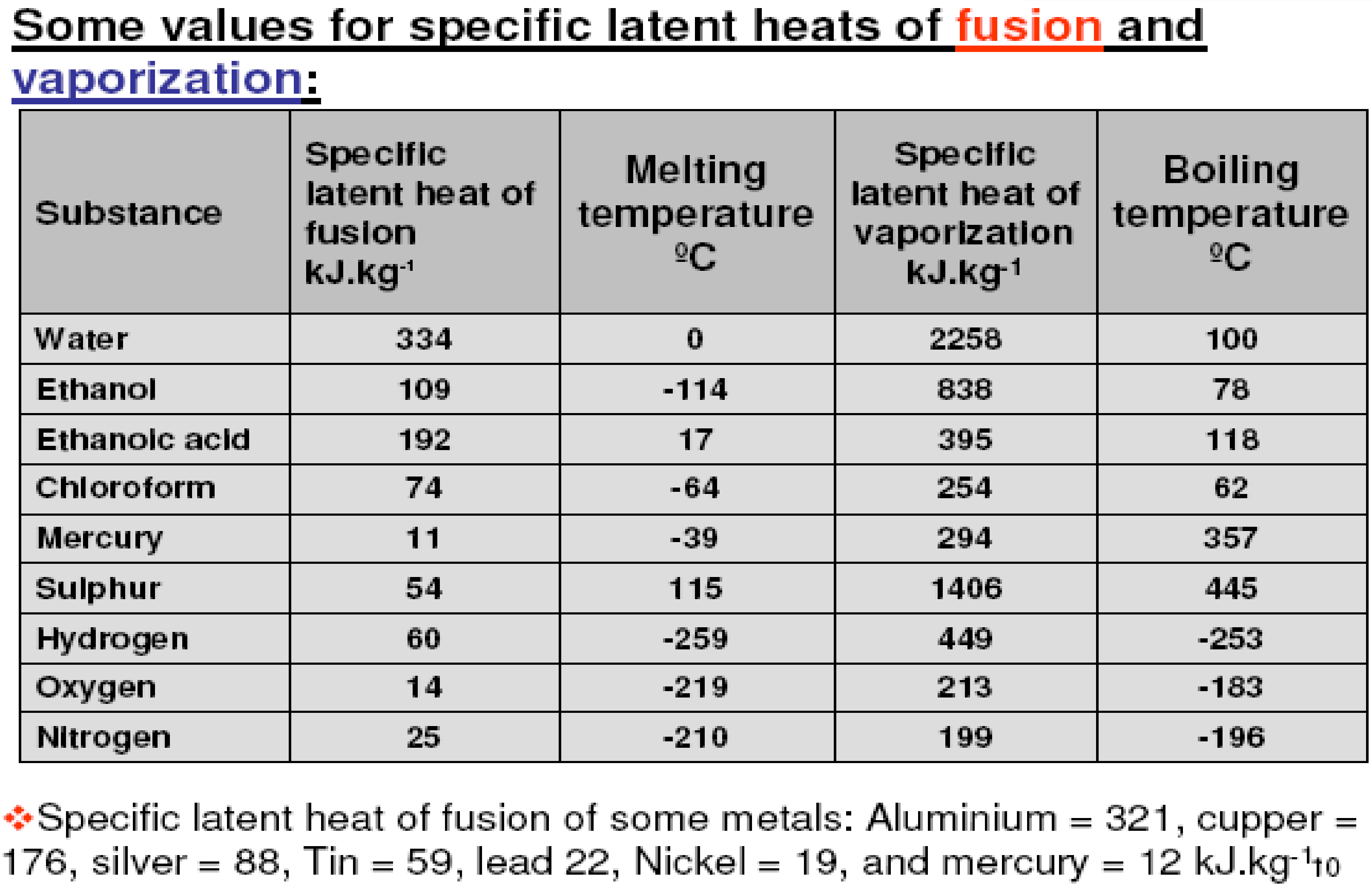
The amount of energy absorbed or released during a phase-change process is called latent heat.

•**Latent heat of fusion** is the amount of energy absorbed during melting.

•**Latent heat of vaporization** is the amount of energy absorbed during vaporization.







Some values for specific latent heats of fusion and vaporization:

Substance	Specific latent heat of fusion kJ.kg^{-1}	Melting temperature ºC	Specific latent heat of vaporization kJ.kg^{-1}	Boiling temperature ºC
Water	334	0	2258	100
Ethanol	109	-114	838	78
Ethanoic acid	192	17	395	118
Chloroform	74	-64	254	62
Mercury	11	-39	294	357
Sulphur	54	115	1406	445
Hydrogen	60	-259	449	-253
Oxygen	14	-219	213	-183
Nitrogen	25	-210	199	-196

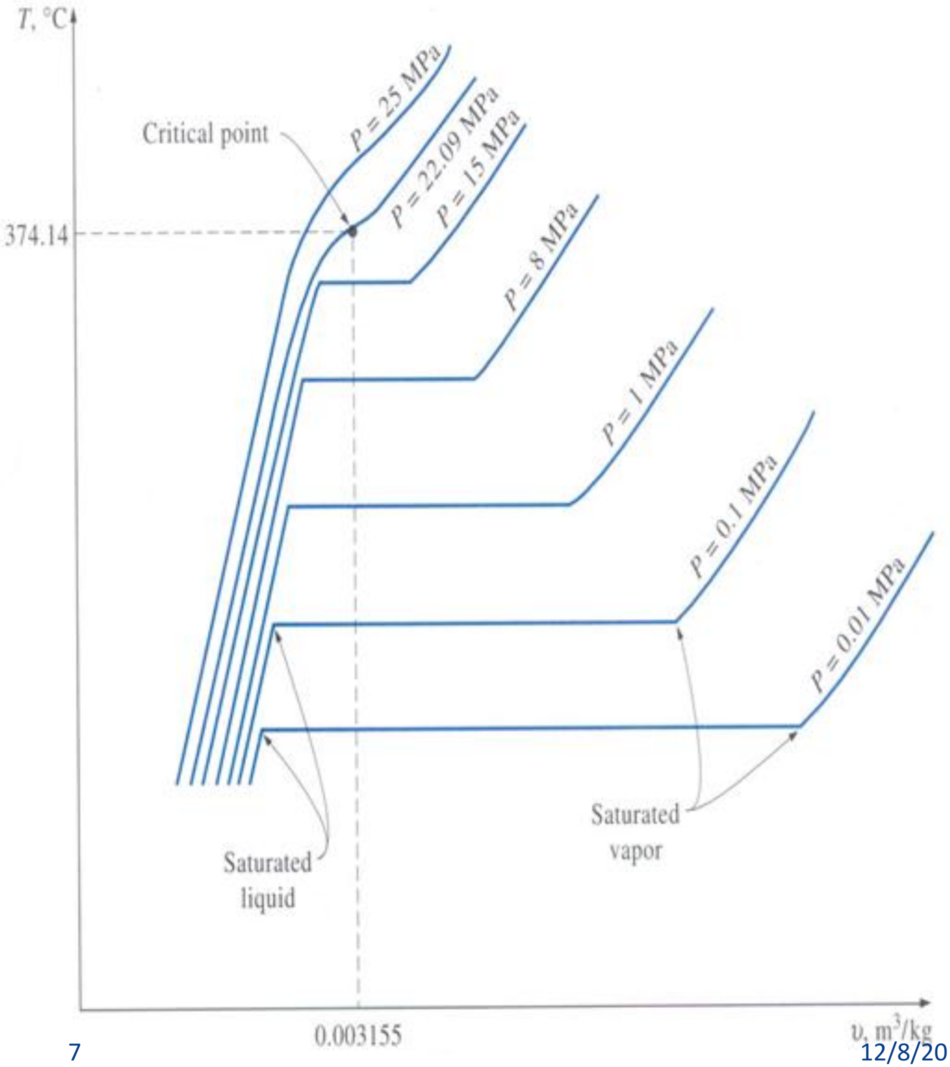
- Specific latent heat of fusion of some metals: Aluminium = 321, cupper = 176, silver = 88, Tin = 59, lead 22, Nickel = 19, and mercury = 12 kJ.kg^{-1}$_{10}$

Property Diagrams for Phase-change Process

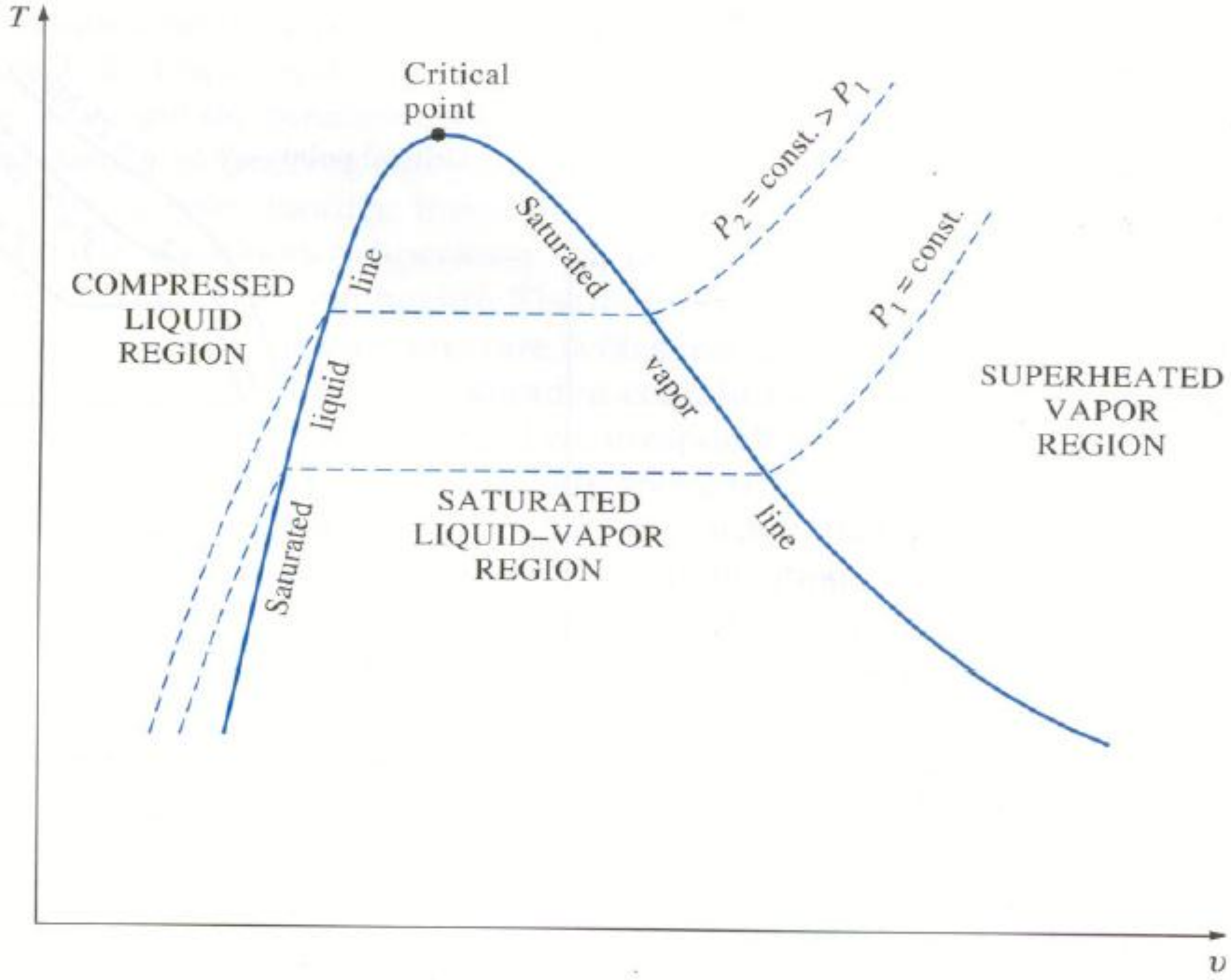
The *T-V* diagram

As pressure increases:

- Water starts boiling at higher temperature
- The specific volume of the saturated liquid becomes larger whereas the specific volume of the saturated vapor becomes smaller.



The *T-V* diagram



Critical point – the saturated liquid and saturated vapor states are identical.

At the *critical point*: $T=T_{cr}$, $P=P_{cr}$, and $v=v_{cr}$.

$\boldsymbol{T_{cr}}$ is the temperature above which a gas cannot be liquefied.

$\boldsymbol{P_{cr}}$ is the pressure that is needed to cause the gas to condense at $\boldsymbol{T_{cr}}$.

At pressure above P_{cr},
there will be no distinct phase change process

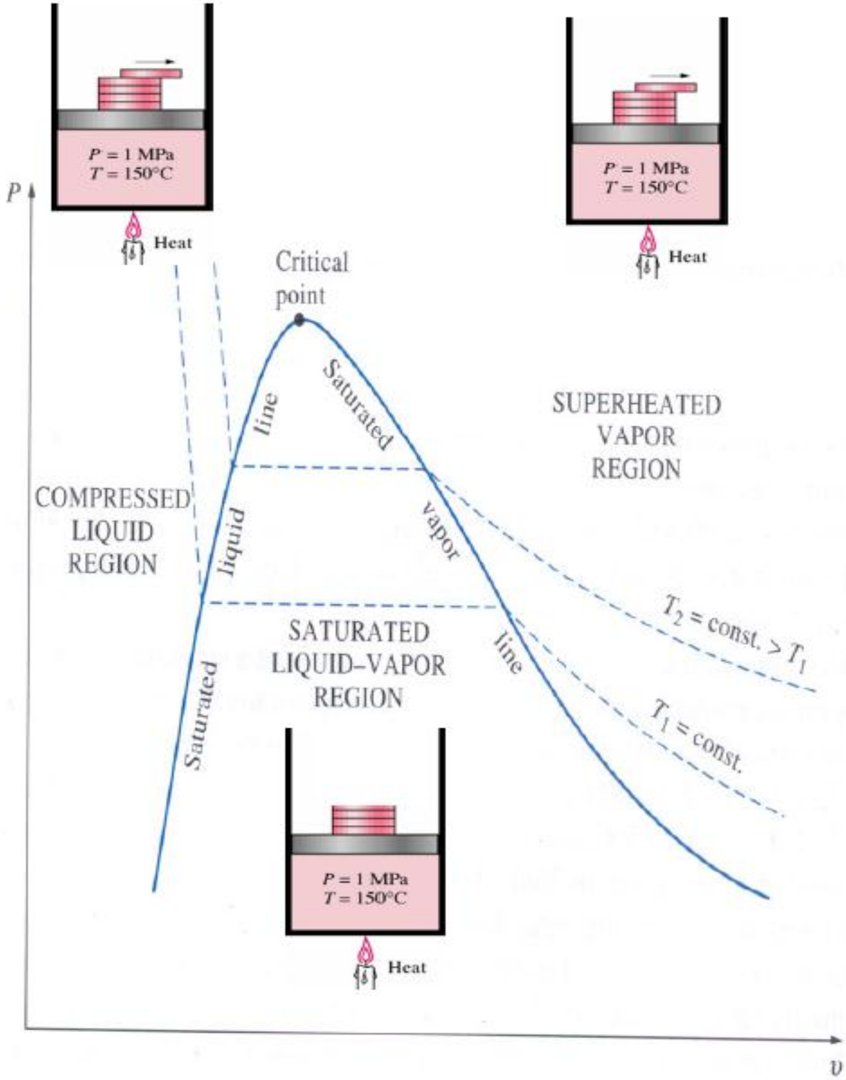
Substances past the critical point are known as ***supercritical fluids*.**

Substance	T_{cr} (K)	P_{cr} (MPa)	v_{cr} ($m^3/kmol$)
Air	132	3.8	0.0883
Nitrogen	126	3.4	0.0899
Oxygen	155	5.1	0.0780
Carbon dioxide	304	7.4	0.0943
Helium	5	0.2	0.0578
Water	647	22.1	0.0568

The *P-v* diagram

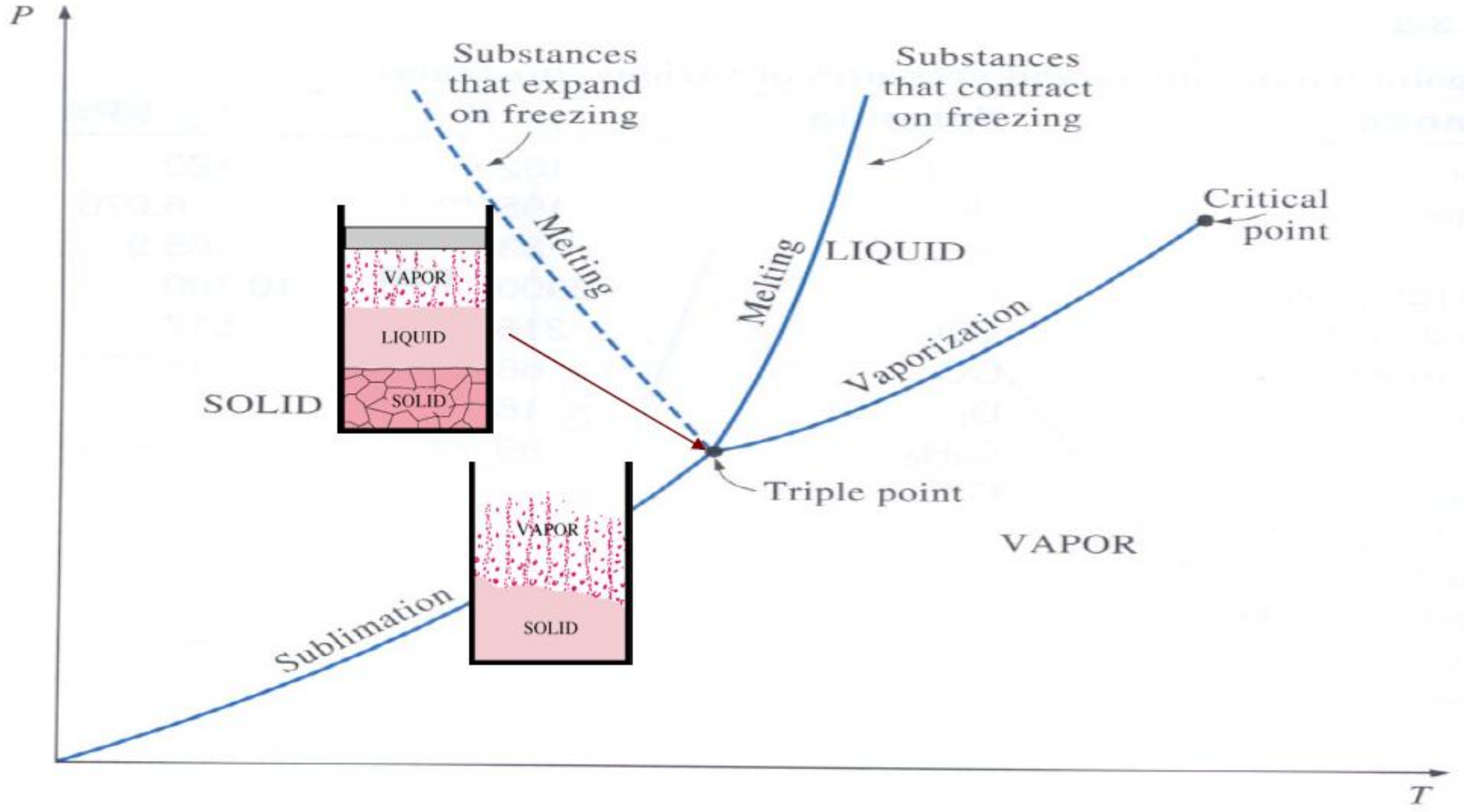
Consider compressed liquid water at 1 MPa and 150 °C.

- When the pressure is reduced to $P_{sat@150C}$ = **0.4758** MPa, the water will start to boil.
- *T* and *P* remain constant during vaporization. Once the last drop is vaporized, *P* decreases whereas *v* increases.



The *P-T* diagram (phase diagram)

The location at which the three phase change border lines meet is called the ***Triple Point.***



- **No substance can exist in the liquid phase at $P < P_{tp}$.**
- **At $P < P_{tp}$, a substance can pass from the solid to vapor phase directly (*sublimation*) without passing through the liquid phase.**
- **For *carbon dioxide* that has a large P_{tp} ($>P_{atm}$) sublimation is the only way to change from the solid to vapor phase at P_{atm}.**

Substance	T_{tp} **(K)**	P_{tp} **(kPa)**
Nitrogen	63.2	12.6
Oxygen	54.4	0.15
Carbon dioxide	216.6	**517**
Helium	2.2	5.1
Water	273.2	0.61

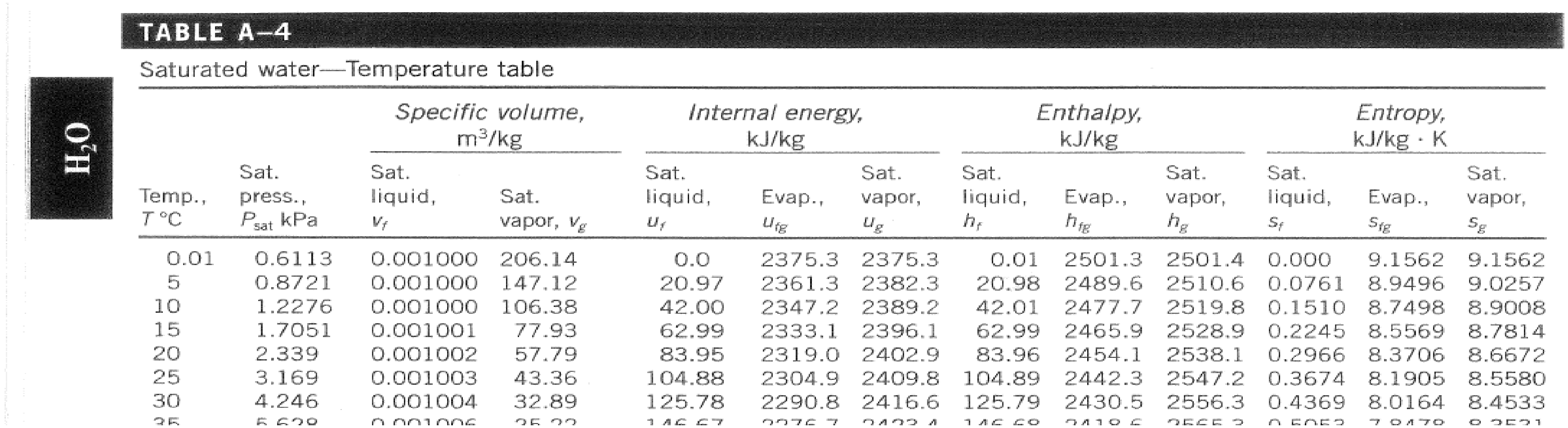
Thermodynamic Property Tables

Important thermodynamic properties are:

- ***Temperature-T***
- ***Pressure-P***
- ***Volume-V (m^3) and specific volume-v (m^3/kg) = V/m***
- ***Internal energy-U,u (kJ, kJ/kg)***
- ***Enthalpy-H,h (kJ, kJ/kg):*** *A combinational Property*

$$H = U + PV \text{ or } h = u + Pv \text{ (kJ)}$$

- **Entropy-*S,s (kJ/K, kJ/kg.K)***: A measure of system disorder



H_2O

TABLE A–4

Saturated water—Temperature table

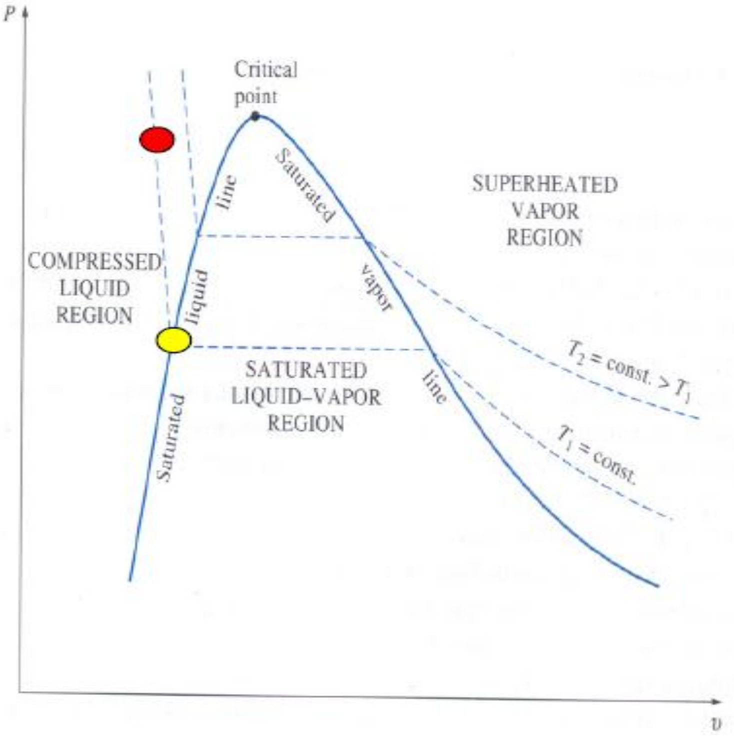
		Specific volume, m³/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg · K		
Temp., T °C	Sat. press., P_{sat} kPa	Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
0.01	0.6113	0.001000	206.14	0.0	2375.3	2375.3	0.01	2501.3	2501.4	0.000	9.1562	9.1562
5	0.8721	0.001000	147.12	20.97	2361.3	2382.3	20.98	2489.6	2510.6	0.0761	8.9496	9.0257
10	1.2276	0.001000	106.38	42.00	2347.2	2389.2	42.01	2477.7	2519.8	0.1510	8.7498	8.9008
15	1.7051	0.001001	77.93	62.99	2333.1	2396.1	62.99	2465.9	2528.9	0.2245	8.5569	8.7814
20	2.339	0.001002	57.79	83.95	2319.0	2402.9	83.96	2454.1	2538.1	0.2966	8.3706	8.6672
25	3.169	0.001003	43.36	104.88	2304.9	2409.8	104.89	2442.3	2547.2	0.3674	8.1905	8.5580
30	4.246	0.001004	32.89	125.78	2290.8	2416.6	125.79	2430.5	2556.3	0.4369	8.0164	8.4533

Compressed Liquid

- Compressed liquid tables are not commonly available.
- This is because of the relative independence of compressed liquid properties from pressure.
- Increasing the pressure 100 times often causes properties to change less than 1 percent.

- A general approximation is to treat compressed liquid as saturated liquid at the given ***temperature***. i.e. $v = vf\ @T$, $u = uf\ @T$, $h = hf\ @\ T$.
- *Characteristics of compressed liquid*:

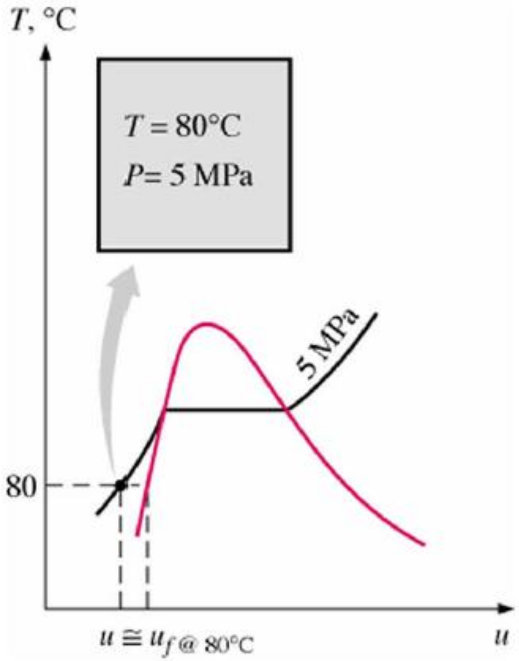
  $P > P_{sat}$ at a given T
  $T < T_{sat}$ at a given P
  $v < v_f$; $u < u_f$; $h < h_f$ at a given T or P



Example 2.1

Determine the internal energy of compressed liquid water at 80 °C and 5 MPa using

- (a) from the compressed liquid table?
- (b) saturated liquid data. What is the error involved in the second case?



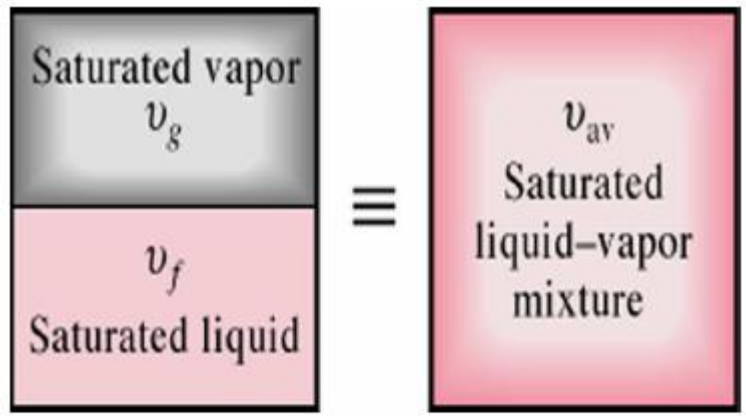
Solution:

- (a) From the compressed liquid table *u* = 333.73 kJ/kg
- (b) From the saturation table at 80 °C *u* = 334.86 kJ/kg

error = (334.86-333.72)/333.72 = 0.34 %

Saturated Liquid-Vapor Mixture

A saturated mixture can be treated as a combination of two subsystems:



Mass fraction of vapor or the *quality*:

$$x = \frac{m_{vapor}}{m_t} = \frac{m_{vapor}}{m_{liquid} + m_{vapor}} = \frac{m_g}{m_f + m_g}$$

- ***x* = 0** for purely saturated liquid
- ***x* = 1** for purely saturated vapor

Average Values: The total volume is the sum of these two:

$$V = V_f + V_g \; ; \; m_t = m_f + m_g$$

$$m_t v_{av} = m_f v_f + m_g v_g = (m_t - m_g)v_f + m_g v_g$$

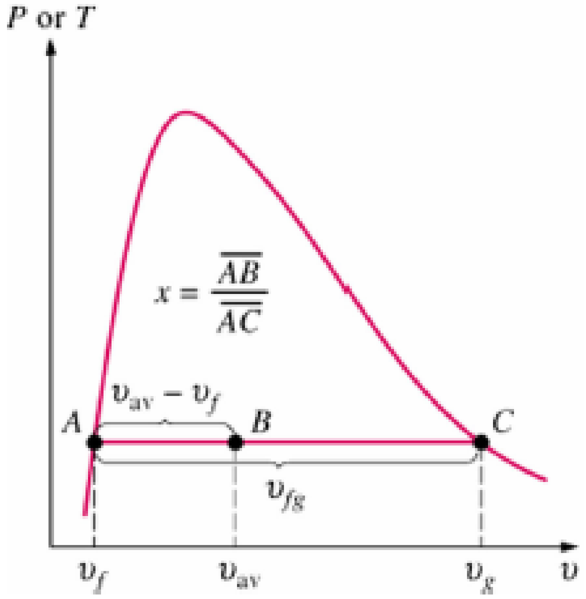
Dividing by m_t yields:

$$v_{av} = (1 - x)v_f + x\, v_g = v_f + x\, v_{fg} \qquad \text{m}^3\text{/kg}$$

Solving for the quality:

$$x = \frac{v_{av} - v_f}{v_{fg}}$$

$$\text{or} \quad v_{av} = v_f + x\, v_{fg} \qquad (m^3/kg)$$



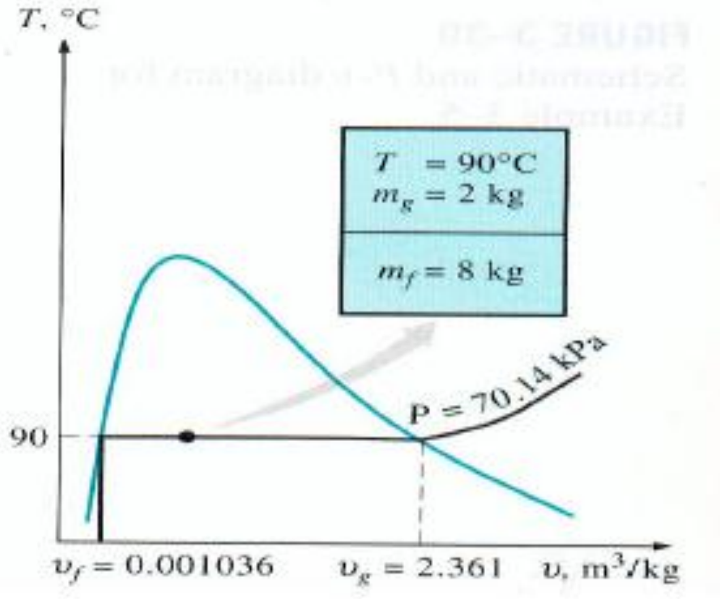
Similarly for internal energy and enthalpy:

$$u_{av} = u_f + x\, u_{fg} \qquad \text{(kJ/kg)}$$

$$h_{av} = h_f + x\, h_{fg} \qquad \text{(kJ/kg)}$$

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.



***Solution*:**

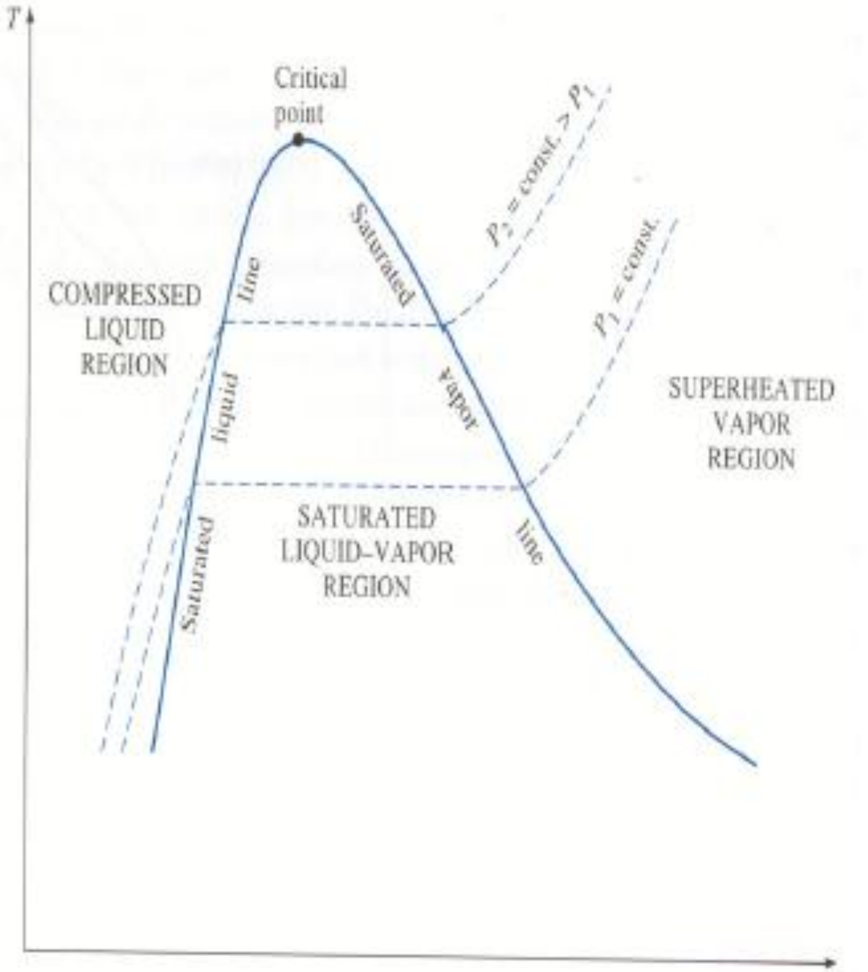
(a) since the two phases coexist in equilibrium:
$P = P_{\text{sat at }90°\text{C}} = 70.14$ kPa (Table 2.4)

(b) $v_f = 0.001036\ \text{m}^3/\text{kg}$; $v_g = 2.361\ \text{m}^3/\text{kg}$ (Table 2.4)

$$V = V_f + V_g$$
$$V = m_f v_f + m_g v_g$$
$$= (8\ \text{kg})(0.0011036\ \text{m}^3/\text{kg}) + (2\ \text{kg})(2.361\ \text{m}^3/\text{kg})$$
$$= 4.73\ \text{m}^3$$

Superheated Vapor

- Since the superheated region is a single-phase region, *temperature and pressure are no longer dependent properties.*

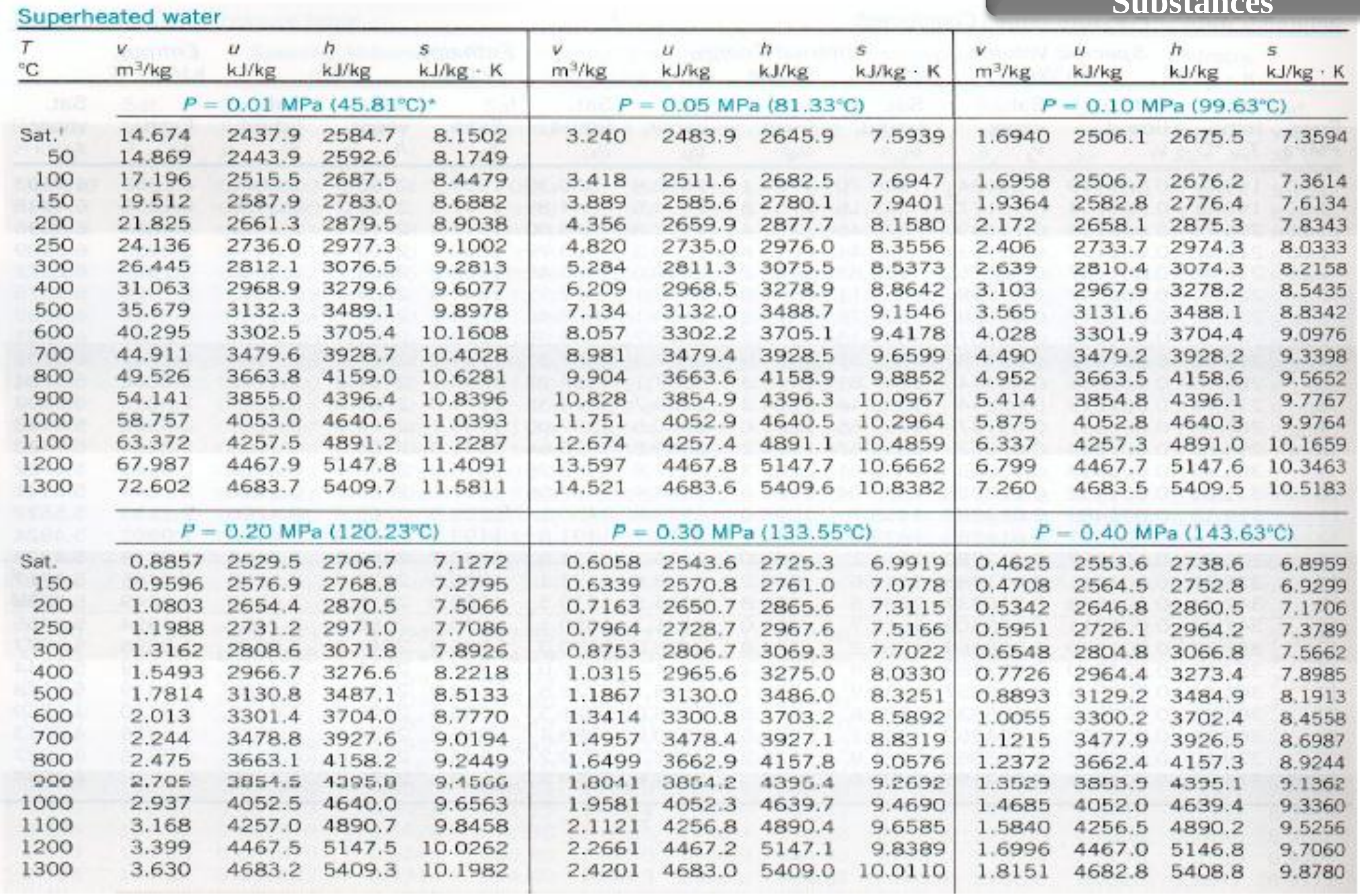


- *Characteristics of superheated vapor*:

  $P<P_{sat}$ at a given T

  $T>T_{sat}$ at a given P

  $v>v_g$; $u>u_g$; $h>h_g$ at a given T or P.



Superheated water

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg · K
	P = 0.01 MPa (45.81°C)*				P = 0.05 MPa (81.33°C)				P = 0.10 MPa (99.63°C)			
Sat.†	14.674	2437.9	2584.7	8.1502	3.240	2483.9	2645.9	7.5939	1.6940	2506.1	2675.5	7.3594
50	14.869	2443.9	2592.6	8.1749								
100	17.196	2515.5	2687.5	8.4479	3.418	2511.6	2682.5	7.6947	1.6958	2506.7	2676.2	7.3614
150	19.512	2587.9	2783.0	8.6882	3.889	2585.6	2780.1	7.9401	1.9364	2582.8	2776.4	7.6134
200	21.825	2661.3	2879.5	8.9038	4.356	2659.9	2877.7	8.1580	2.172	2658.1	2875.3	7.8343
250	24.136	2736.0	2977.3	9.1002	4.820	2735.0	2976.0	8.3556	2.406	2733.7	2974.3	8.0333
300	26.445	2812.1	3076.5	9.2813	5.284	2811.3	3075.5	8.5373	2.639	2810.4	3074.3	8.2158
400	31.063	2968.9	3279.6	9.6077	6.209	2968.5	3278.9	8.8642	3.103	2967.9	3278.2	8.5435
500	35.679	3132.3	3489.1	9.8978	7.134	3132.0	3488.7	9.1546	3.565	3131.6	3488.1	8.8342
600	40.295	3302.5	3705.4	10.1608	8.057	3302.2	3705.1	9.4178	4.028	3301.9	3704.4	9.0976
700	44.911	3479.6	3928.7	10.4028	8.981	3479.4	3928.5	9.6599	4.490	3479.2	3928.2	9.3398
800	49.526	3663.8	4159.0	10.6281	9.904	3663.6	4158.9	9.8852	4.952	3663.5	4158.6	9.5652
900	54.141	3855.0	4396.4	10.8396	10.828	3854.9	4396.3	10.0967	5.414	3854.8	4396.1	9.7767
1000	58.757	4053.0	4640.6	11.0393	11.751	4052.9	4640.5	10.2964	5.875	4052.8	4640.3	9.9764
1100	63.372	4257.5	4891.2	11.2287	12.674	4257.4	4891.1	10.4859	6.337	4257.3	4891.0	10.1659
1200	67.987	4467.9	5147.8	11.4091	13.597	4467.8	5147.7	10.6662	6.799	4467.7	5147.6	10.3463
1300	72.602	4683.7	5409.7	11.5811	14.521	4683.6	5409.6	10.8382	7.260	4683.5	5409.5	10.5183
	P = 0.20 MPa (120.23°C)				P = 0.30 MPa (133.55°C)				P = 0.40 MPa (143.63°C)			
Sat.	0.8857	2529.5	2706.7	7.1272	0.6058	2543.6	2725.3	6.9919	0.4625	2553.6	2738.6	6.8959
150	0.9596	2576.9	2768.8	7.2795	0.6339	2570.8	2761.0	7.0778	0.4708	2564.5	2752.8	6.9299
200	1.0803	2654.4	2870.5	7.5066	0.7163	2650.7	2865.6	7.3115	0.5342	2646.8	2860.5	7.1706
250	1.1988	2731.2	2971.0	7.7086	0.7964	2728.7	2967.6	7.5166	0.5951	2726.1	2964.2	7.3789
300	1.3162	2808.6	3071.8	7.8926	0.8753	2806.7	3069.3	7.7022	0.6548	2804.8	3066.8	7.5662
400	1.5493	2966.7	3276.6	8.2218	1.0315	2965.6	3275.0	8.0330	0.7726	2964.4	3273.4	7.8985
500	1.7814	3130.8	3487.1	8.5133	1.1867	3130.0	3486.0	8.3251	0.8893	3129.2	3484.9	8.1913
600	2.013	3301.4	3704.0	8.7770	1.3414	3300.8	3703.2	8.5892	1.0055	3300.2	3702.4	8.4558
700	2.244	3478.8	3927.6	9.0194	1.4957	3478.4	3927.1	8.8319	1.1215	3477.9	3926.5	8.6987
800	2.475	3663.1	4158.2	9.2449	1.6499	3662.9	4157.8	9.0576	1.2372	3662.4	4157.3	8.9244
900	2.705	3854.5	4395.8	9.4566	1.8041	3854.2	4395.4	9.2692	1.3529	3853.9	4395.1	9.1362
1000	2.937	4052.5	4640.0	9.6563	1.9581	4052.3	4639.7	9.4690	1.4685	4052.0	4639.4	9.3360
1100	3.168	4257.0	4890.7	9.8458	2.1121	4256.8	4890.4	9.6585	1.5840	4256.5	4890.2	9.5256
1200	3.399	4467.5	5147.5	10.0262	2.2661	4467.2	5147.1	9.8389	1.6996	4467.0	5146.8	9.7060
1300	3.630	4683.2	5409.3	10.1982	2.4201	4683.0	5409.0	10.0110	1.8151	4682.8	5408.8	9.8780

Example

Determine the temperature of water at a state of $P = 0.5$ MPa and $h = 2890$ kJ/kg.

Solution:

At 0.5 MPa, the enthalpy of the saturated vapor is $h_g = 2748.7$ kJ/kg.
Since $h > h_g$ =>, it is **a superheated vapor**.

Under 0.50 MPa in the following table we read that:
At $T = 200^{\circ}\text{C}$, $h = 2855.4$ kJ/kg,
and at $T = 250^{\circ}\text{C}$, $h = 2960.7$ kJ/kg.

Thus T is between 200ºC and 250ºC. By linear interpolation,

$$T = 216.4^{\circ}\text{C}$$

The Ideal-Gas Equation of State - history

- The pressure of gases is *inversely proportional* to their volume (for a fixed mass of gas at a constant temperature *T*).

$$V = f(T) / P$$

Robert Boyle, Irish physicist and chemist, c 1670s.

- At a constant (but low) pressure the volume of a gas is *proportional* to its temperature.

$$V / T = f'(P)$$

Jacques A. C. Charles in 1787,

- under conditions of the same temperature and pressure, equal volumes of all gases contained equal number of molecules.

$$V = n f''(P, T)$$

Amedeo Avogadro (1776-1856):

The Ideal-Gas Equation of State

Any equation that relates the pressure, temperature, and specific volume of a substance (or whatever else) is an *equation of state.*

Ideal-gas equation of state:

$$PV = mRT$$

or $Pv = RT$ $\qquad v = V/m$

or $P = \rho RT$ $\qquad \rho = 1/v$

R = gas constant which is different for each gas (in kJ/kg.K or kPa.m^3/kg.K)

P = absolute pressure (in kPa)

T = absolute temperature (in K)

m = mass (in kg)

v = specific volume (v = V/m) in kg/m3

r = density (= 1/ *v) in m3/kg*

In terms of mass:

$$PV = mRT$$

In terms of mole:

$$PV = nR_uT$$

so:

$nR_u = mR \qquad R_u = R(m/n) = RM$

n = number of moles

M = the molar mass (mass of one mole) or molecular weight (*m = nM*)

Ru = universal gas constant = 8.314 kJ/kmol.K = 8.314 kPa m^3/kmol.K

Note:-

- ✓ Many familiar gases such as ***air, nitrogen, oxygen, hydrogen, helium, argon,*** ***and*** ***carbon dioxide*** follow the ideal gas relation with negligible error (less than 1 percent).
- ✓ Dense gases such as ***water vapor*** should not be treated as ideal gases.

Is water vapor an ideal gas?

At pressure below 10 kPa, water vapor can be treated as an ideal gas, regardless of Temperature

No – high pressure steam in power plant applications

Yes – air conditioning applications

Compressibility Factor (*Z)*

$$Z = \frac{Pv}{RT} = \frac{v_{actual}}{v_{ideal}} \qquad (v_{\text{ideal}} = RT/P)$$

Z is a measure of deviation from Ideal-gas behavior.

Z = 1, ideal gas

Z <> 1, non-ideal or real gas

- *Experimental finding: Gases behave differently at a given* temperature and pressure, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures.

The generalized compressibility chart

PR = reduced pressure

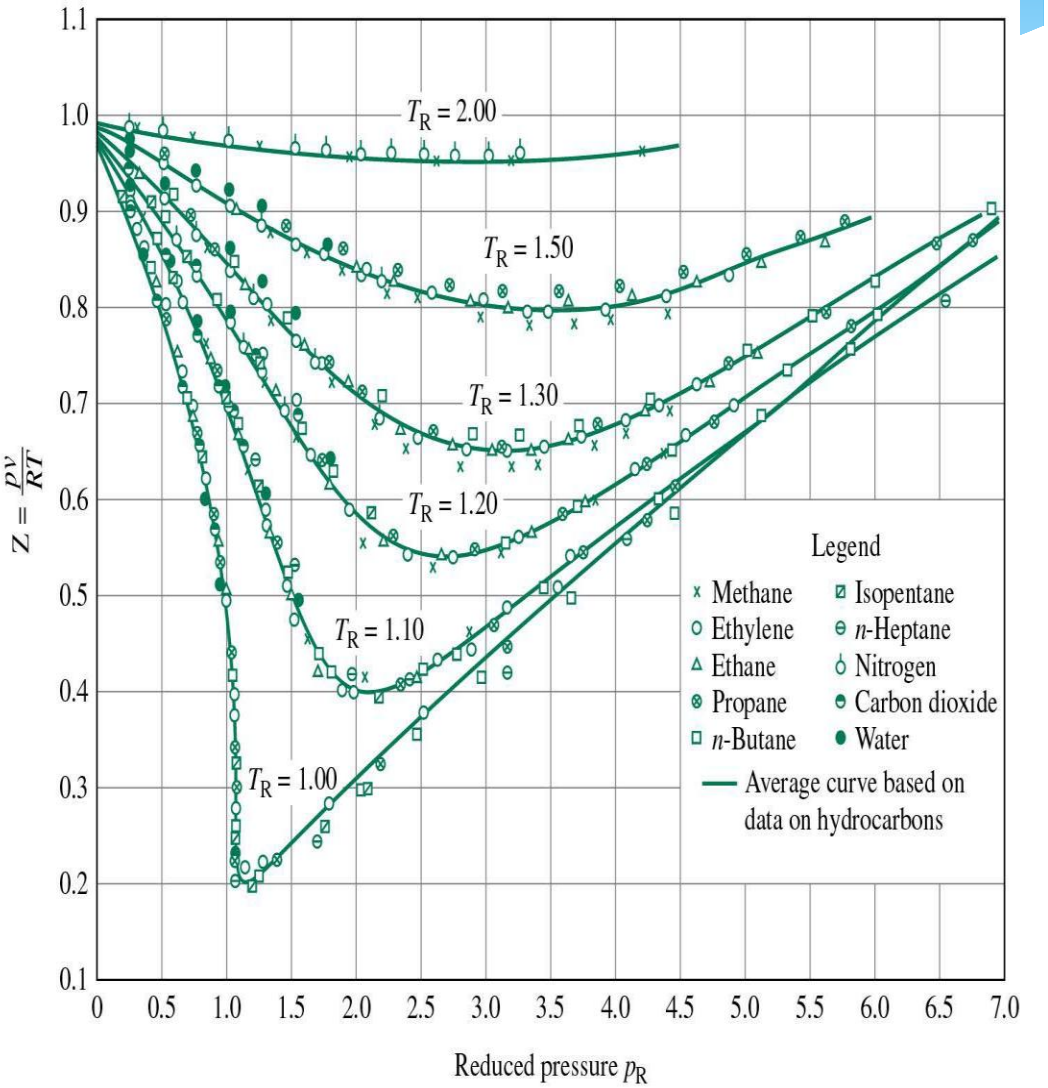
$$P_R = \frac{P}{P_{cr}}$$

TR = reduced temperature

$$T_R = \frac{T}{T_{cr}}$$

v*$_R$ *= pseudo-reduced specific volume

$$v_R = \frac{v_{actual}}{RT_{cr} / P_{cr}}$$



Example

Determine the pressure of water vapor at 300 °C and 0.08114 m3/kg using

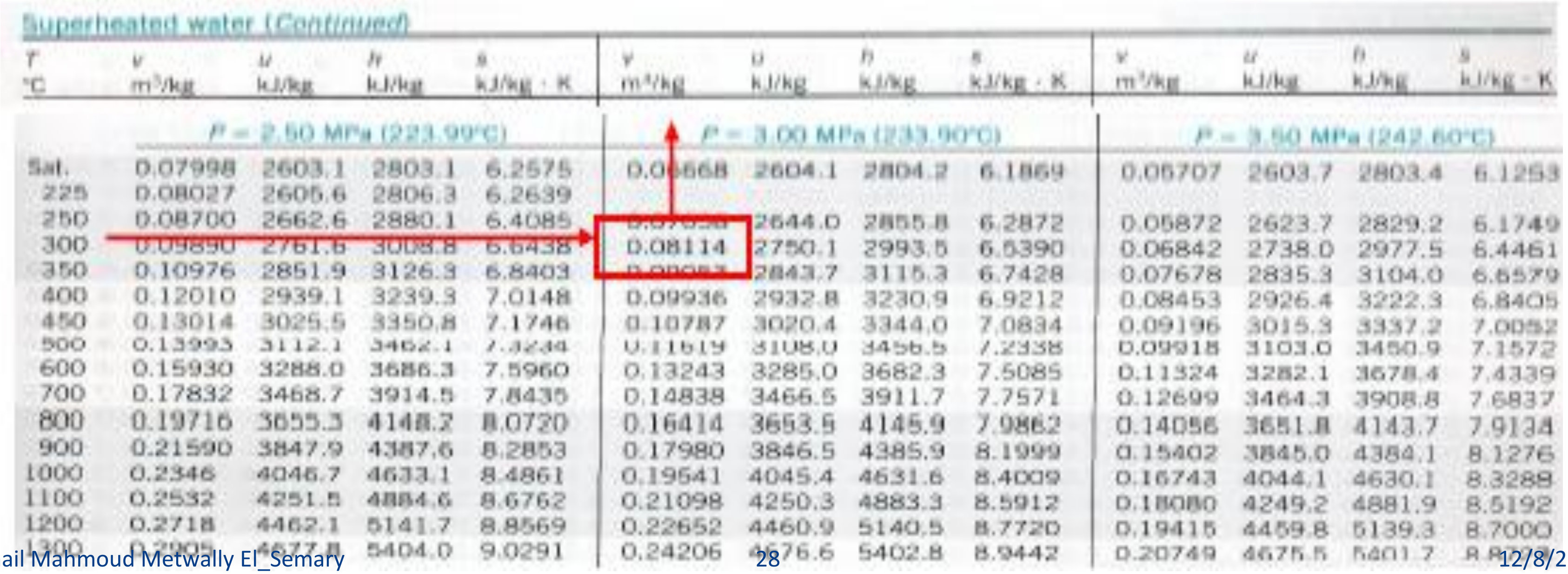
a) steam table,

b) the ideal gas equation (*R=0.4615 kJ/kg.K)*

c) the generalized compressibility chart.

Solution:

a) From the table, *P = 3.0 MPa. This is the experimentally* determined value.



Superheated water (*Continued*)

T °C	*v* m³/kg	*u* kJ/kg	*h* kJ/kg	*s* kJ/kg · K	*v* m³/kg	*u* kJ/kg	*h* kJ/kg	*s* kJ/kg · K	*v* m³/kg	*u* kJ/kg	*h* kJ/kg	*s* kJ/kg · K
	P = 2.50 MPa (223.99°C)				*P* = 3.00 MPa (233.90°C)				*P* = 3.50 MPa (242.60°C)			
Sat.	0.07998	2603.1	2803.1	6.2575	0.06668	2604.1	2804.2	6.1869	0.05707	2603.7	2803.4	6.1253
225	0.08027	2605.6	2806.3	6.2639								
250	0.08700	2662.6	2880.1	6.4085	0.07058	2644.0	2855.8	6.2872	0.05872	2623.7	2829.2	6.1749
300	0.09890	2761.6	3008.8	6.6438	0.08114	2750.1	2993.5	6.5390	0.06842	2738.0	2977.5	6.4461
350	0.10976	2851.9	3126.3	6.8403	0.09053	2843.7	3115.3	6.7428	0.07678	2835.3	3104.0	6.6579
400	0.12010	2939.1	3239.3	7.0148	0.09936	2932.8	3230.9	6.9212	0.08453	2926.4	3222.3	6.8405
450	0.13014	3025.5	3350.8	7.1746	0.10787	3020.4	3344.0	7.0834	0.09196	3015.3	3337.2	7.0052
500	0.13993	3112.1	3462.1	7.3234	0.11619	3108.0	3456.5	7.2338	0.09918	3103.0	3450.9	7.1572
600	0.15930	3288.0	3686.3	7.5960	0.13243	3285.0	3682.3	7.5085	0.11324	3282.1	3678.4	7.4339
700	0.17832	3468.7	3914.5	7.8435	0.14838	3466.5	3911.7	7.7571	0.12699	3464.3	3908.8	7.6837
800	0.19716	3655.3	4148.2	8.0720	0.16414	3653.5	4145.9	7.9862	0.14056	3651.8	4143.7	7.9134
900	0.21590	3847.9	4387.6	8.2853	0.17980	3846.5	4385.9	8.1999	0.15402	3845.0	4384.1	8.1276
1000	0.2346	4046.7	4633.1	8.4861	0.19541	4045.4	4631.6	8.4009	0.16743	4044.1	4630.1	8.3288
1100	0.2532	4251.5	4884.6	8.6762	0.21098	4250.3	4883.3	8.5912	0.18080	4249.2	4881.9	8.5192
1200	0.2718	4462.1	5141.7	8.8569	0.22652	4460.9	5140.5	8.7720	0.19415	4459.8	5139.3	8.7000
1300	0.2905	4677.8	5404.0	9.0291	0.24206	4676.6	5402.8	8.9442	0.20749	4675.5	5401.7	[illegible]

b) ***Ideal gas***

P = RT/v = (0.4615 kJ/kg.K) ×(573.15 K)/(0.08114 m3/kg)
P =3,260 kPa = ***3.26 MPa***

c) ***Real gas***

For water: ***Tcr = 647.3 K; Pcr = 22.09 MPa***
TR = T / Tcr = 573/647.3 = 0.89

$$v_R = \frac{v_{actual}}{RT_{cr}/P_{cr}} = \frac{0.08114 \times 22090}{0.4614 \times 647.3} = 6.0$$

From the chart *PR = 0.135*
P= PR × Pcr = 0.135 × 22.09 = ***2.98 MPa***

Van der Waals Equation of State:-

1837-1927

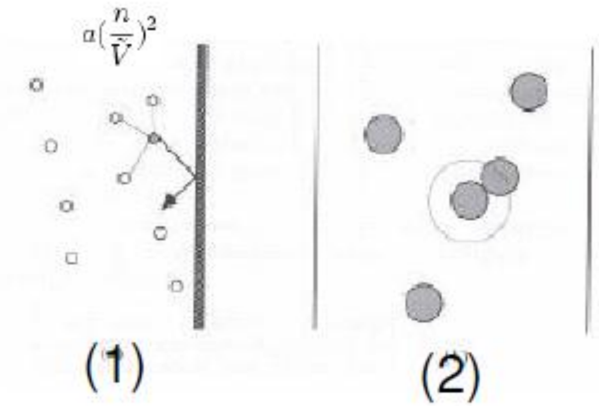
Considers

(1) the intermolecular attraction forces

(2) the volume occupied by molecules themselves.

$$\left(P+\frac{a}{v^2}\right)(v-b)=RT$$

Thus, the first and second derivatives of *P with respect to v at* the critical point must be zero.



$$\left(\frac{\partial P}{\partial v}\right)_{T=T_{cr}}=0 \text{ and } \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_{cr}}=0$$

$$a=\frac{27R^2T_{cr}^2}{64P_{cr}} \text{ and } b=\frac{RT_{cr}}{8P_{cr}}$$

Example

Predict the pressure of nitrogen gas at 175 K and *v* = 0.00375 m3/kg on the basis of
(a) the ideal-gas equation of state
(b) the van der Waals equation of state (*a and b are* given).
Compare the values obtained to the experimentally determined value of 10,000 kPa.

Solution

a)

P = RT/v

= (0.2968 kPa m3/kg K)(175 K)/(0.00375 m3/kg)

P = 13,851 kPa

which is error by 38.5 %

b)

$$P = RT/(v-b) - a/v^2$$

$$a = \frac{27R^2T_{cr}^2}{64P_{cr}} = 0.175\ \mathrm{m}^6 kP/kg^2 \qquad b = \frac{RT_{cr}}{8P_{cr}} = 0.000138\ \mathrm{m}^3/kg$$

P = 9,471 kPa

which is error by 5.3 %

Some other properties of pure substances

- ***Density - mass per unit*** volume (mL-3)

ρ= *m/V (kg/m3)*

For *liquids the effect on the* density by variations in pressure and temperature is generally small.

- ***Specific weight - weight per unit volume (FL-3)***

$$\gamma = \rho g \ (\mathrm{kg/m^3} \times \mathrm{m/s^2} = \mathrm{N/m^3})$$

- ***Specific Gravity - the ratio of the density of a substance*** to the density of some standard substance at a specified temperature, usually water at 4 °C.

$$SG = \rho/\rho_{water} \text{ at } 4°\mathrm{C}$$

- ***Specific Heat- The specific heat is the amount of energy*** *per unit mass required to raise the temperature by one degree Celsius.*
  - The value of *C depends on the nature of the process* undergone during the energy transfer.

Cv: at a constant volume

Cp: at a constant pressure

- For liquids and solids *Cv = Cp = C.*
- For gases *Cp > Cv.*

- *Definitions of Cv and Cp for real gas:*

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v \qquad C_P = \left(\frac{\partial h}{\partial T}\right)_P$$