CH2303 Chemical Engineering Thermodynamics I

Unit – III

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PVT Behavior of Fluids

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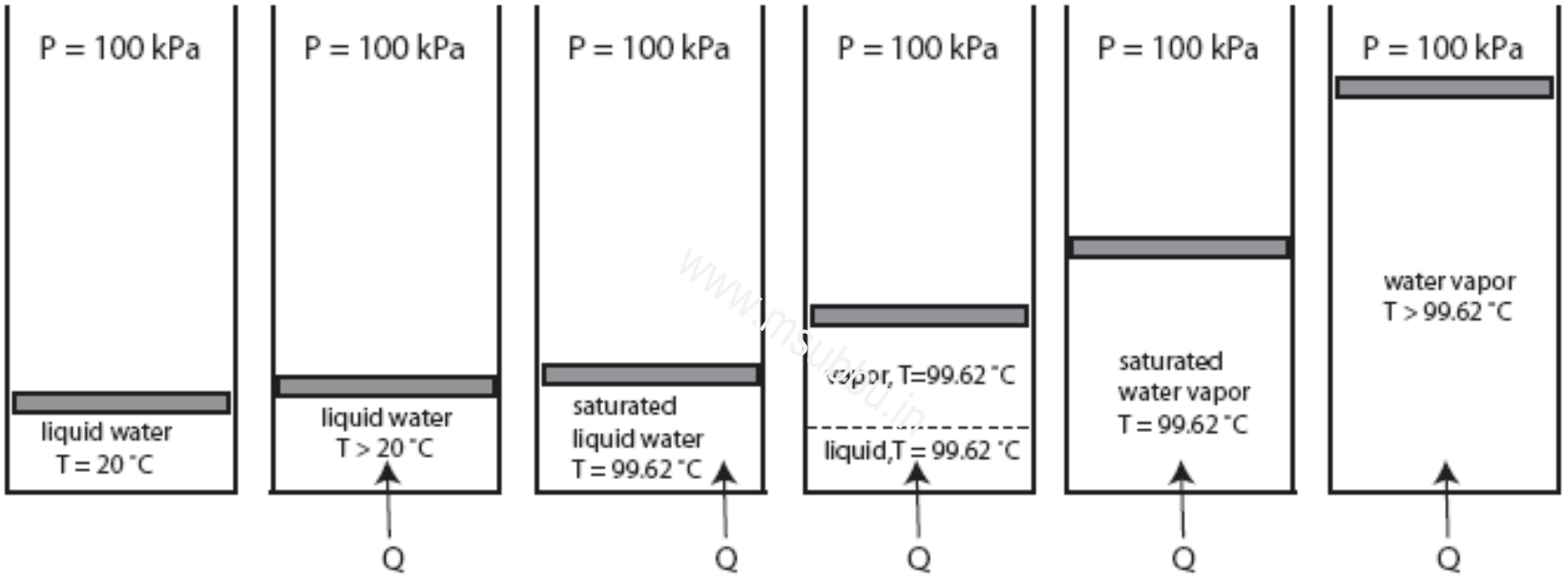
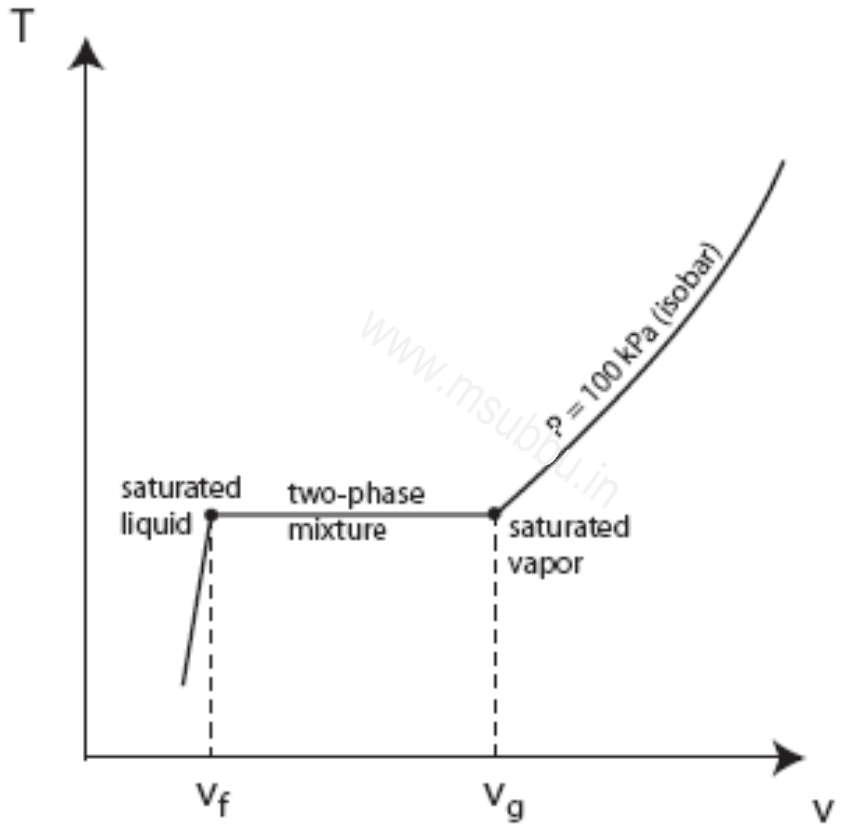
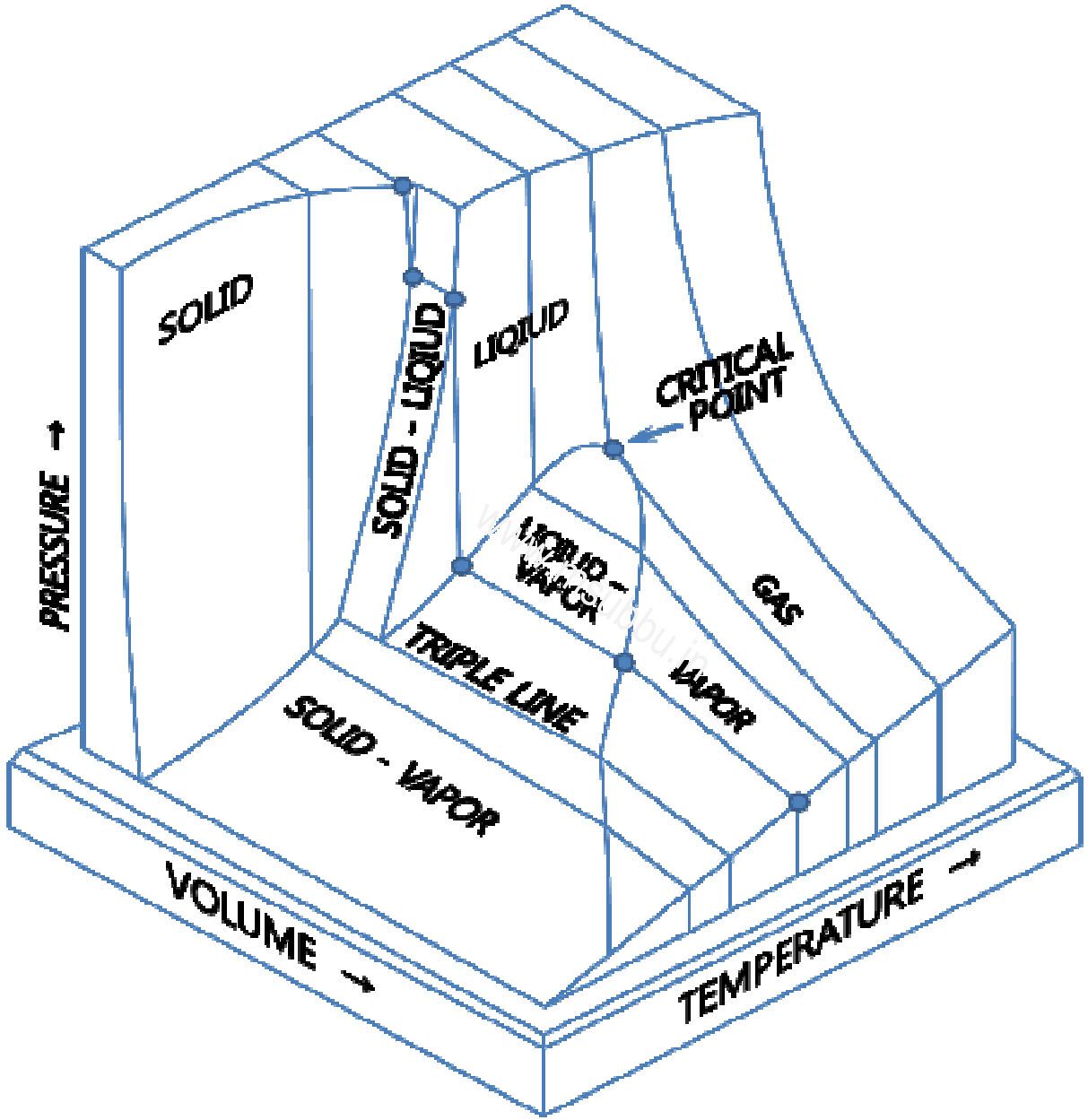
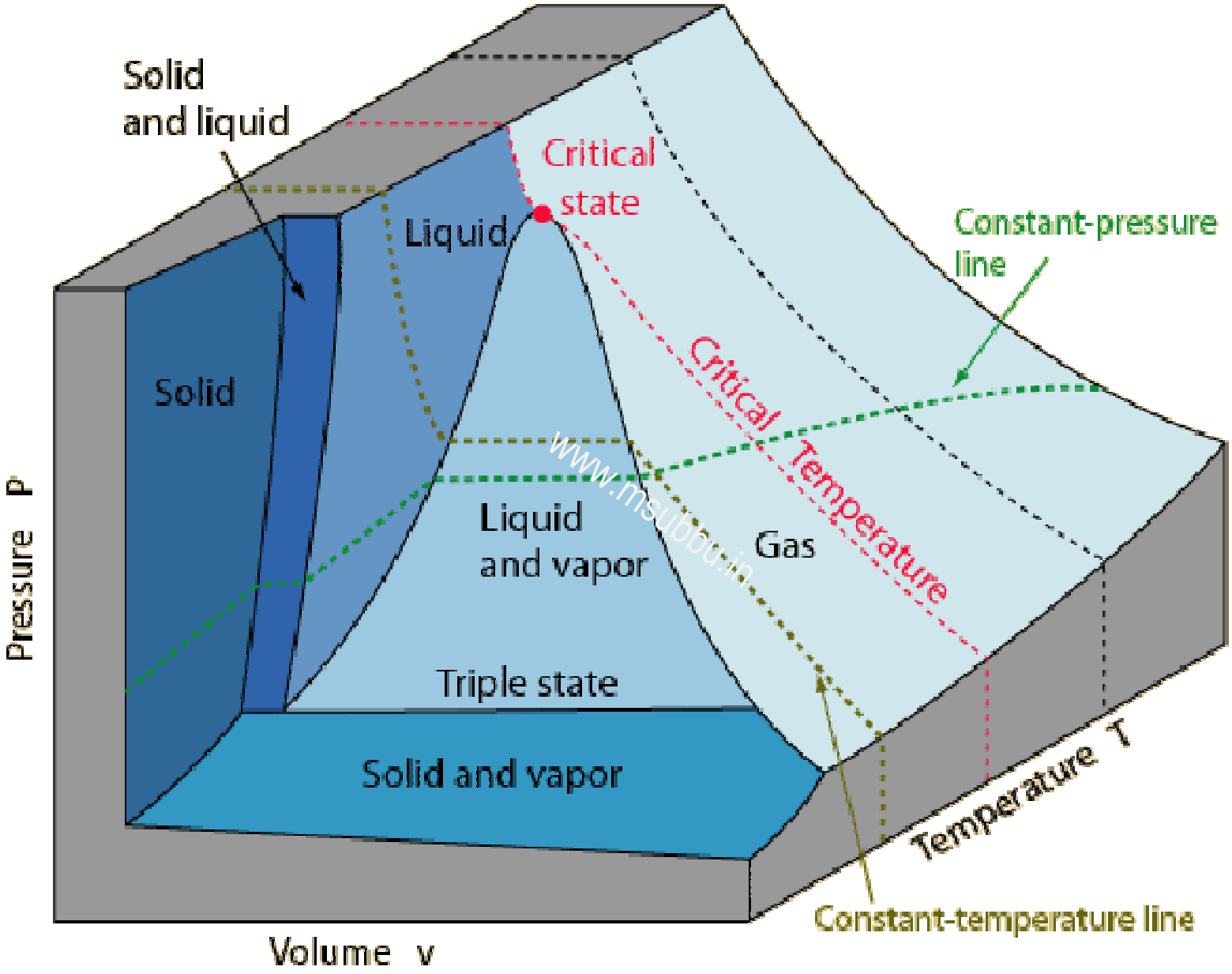
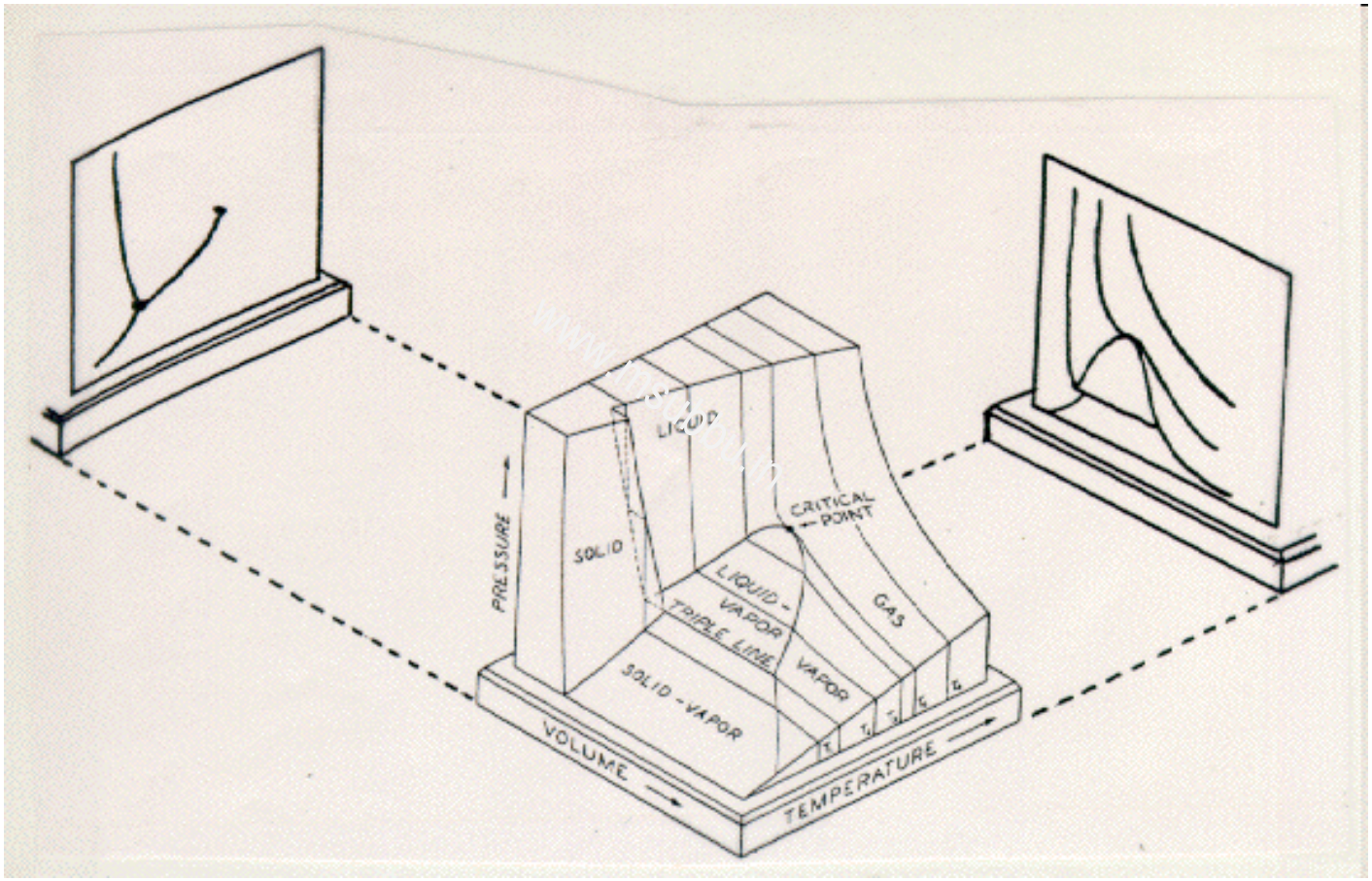


Figure 3.2: Sketch of experiment in which heat is added isobarically to water in a *closed* piston-cylinder arrangement.

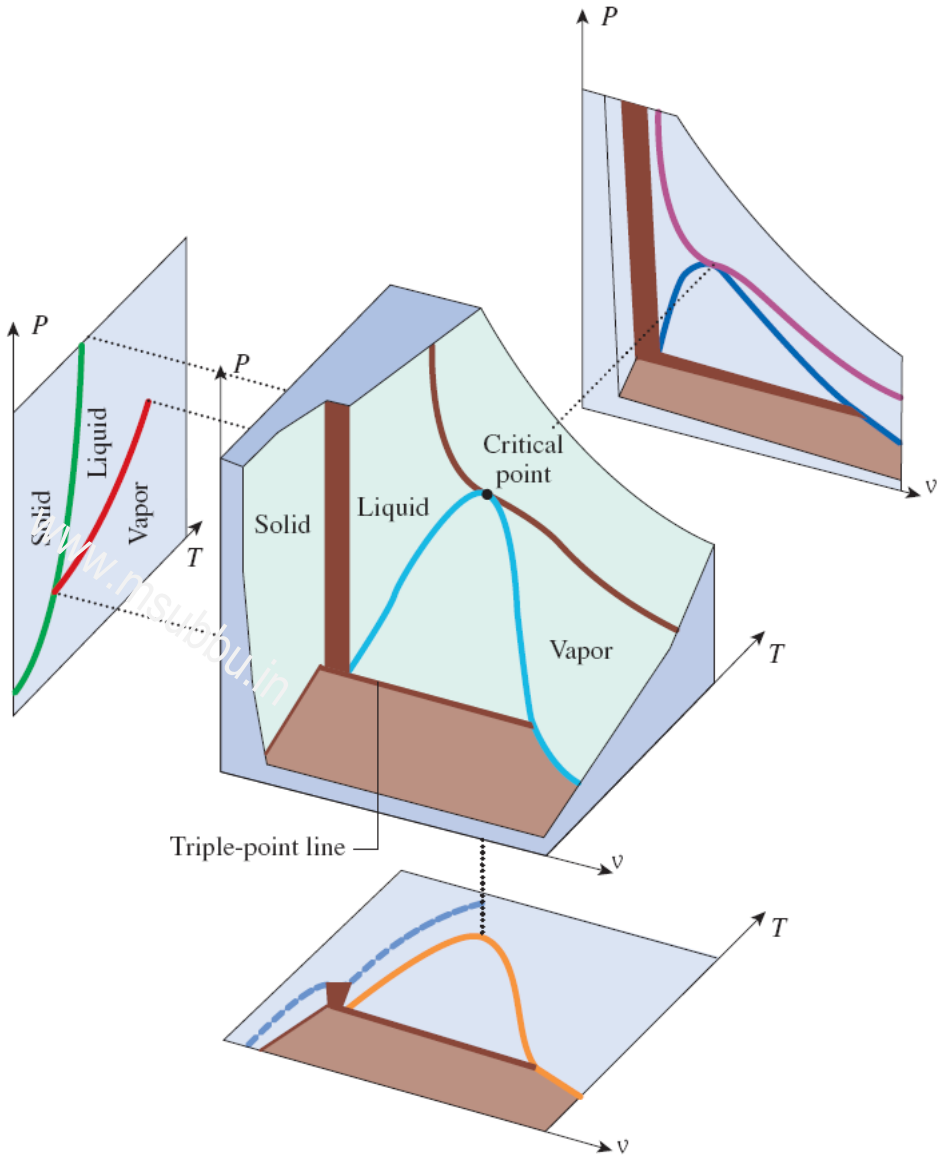

T
P = 100 kPa (isobar)
saturated
liquid
two-phase
mixture
saturated
vapor
v_f
v_g
v

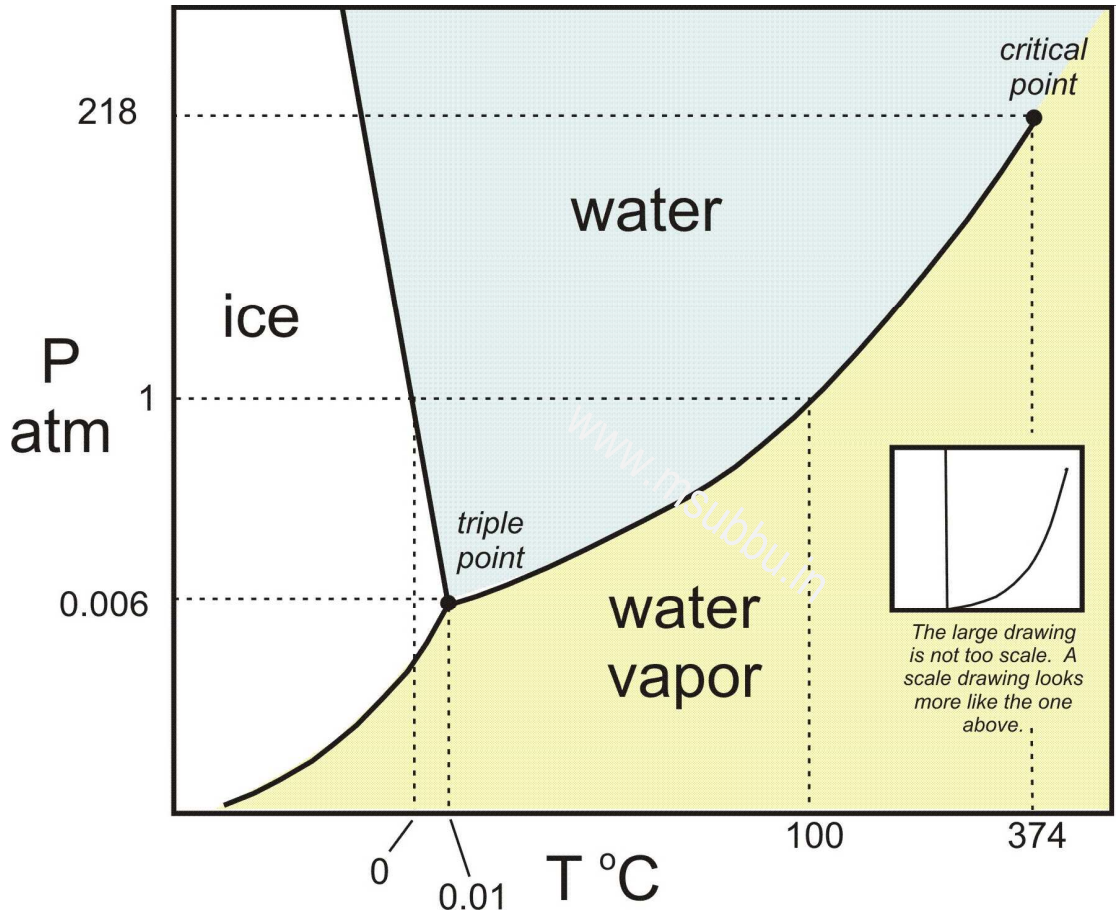

SOLID
SOLID - LIQUID
LIQUID
CRITICAL POINT
LIQUID - VAPOR
GAS
TRIPLE LINE
VAPOR
SOLID - VAPOR
PRESSURE →
VOLUME →
TEMPERATURE →


Solid
and liquid
Critical
state
Liquid
Constant-pressure
line
Solid
Critical Temperature
Liquid
and vapor
Gas
Triple state
Solid and vapor
Pressure p
Volume v
Temperature T
Constant-temperature line


LIQUID
CRITICAL POINT
SOLID
LIQUID - VAPOR
GAS
TRIPLE LINE
VAPOR
SOLID - VAPOR
PRESSURE
VOLUME
TEMPERATURE

PVT surface for a substance that contacts upon freezing

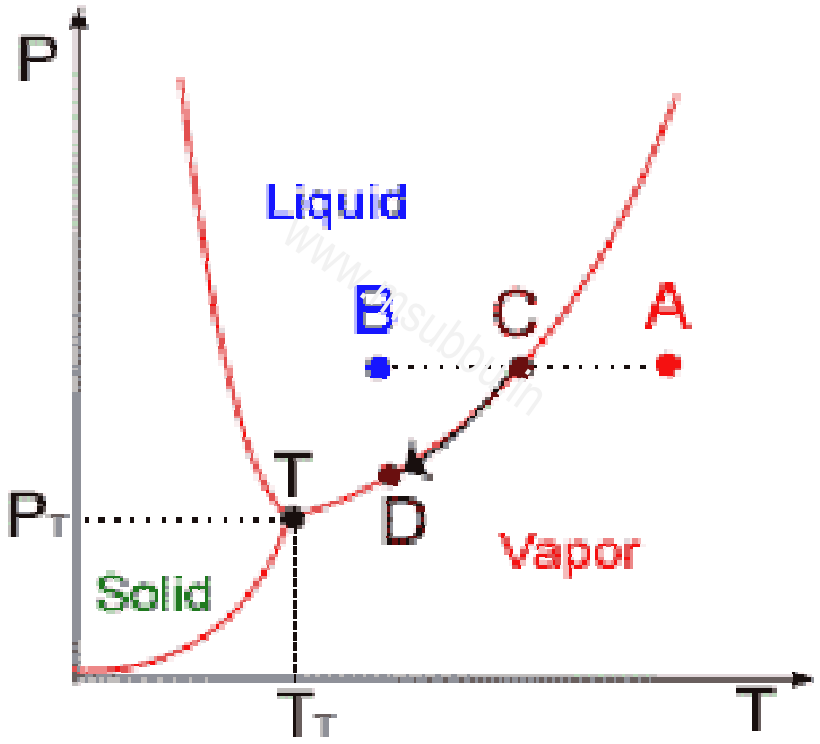


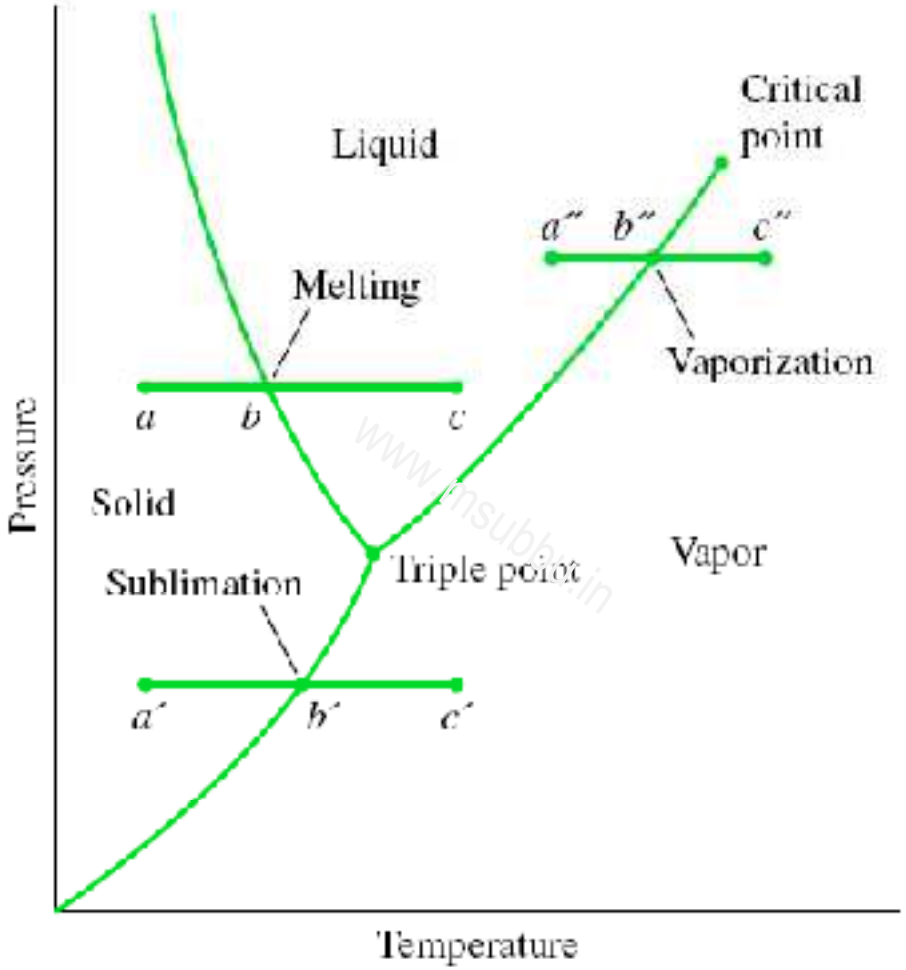


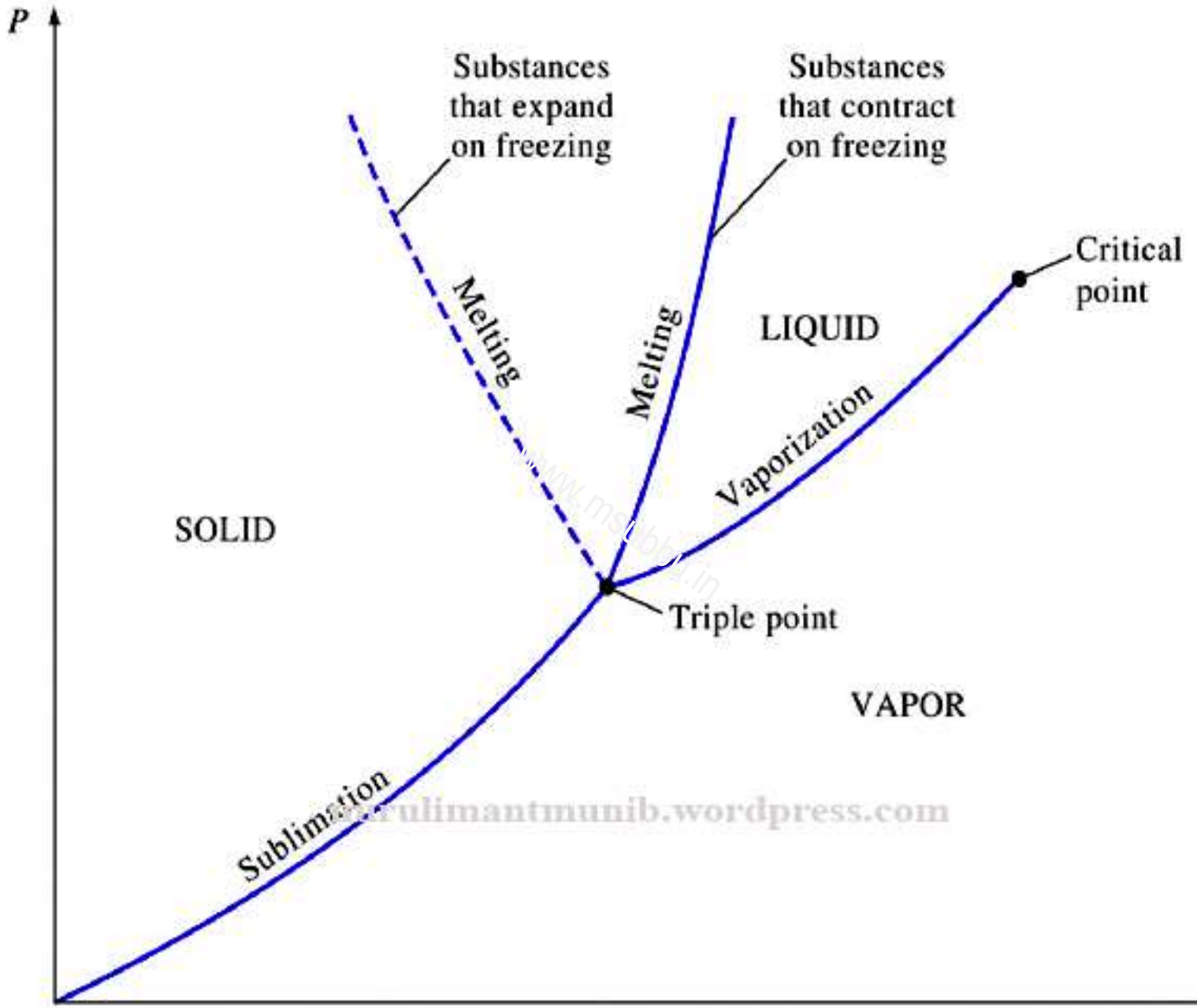
Triple point: P = 611.7 N/m^2; T = 0.01^{o}C

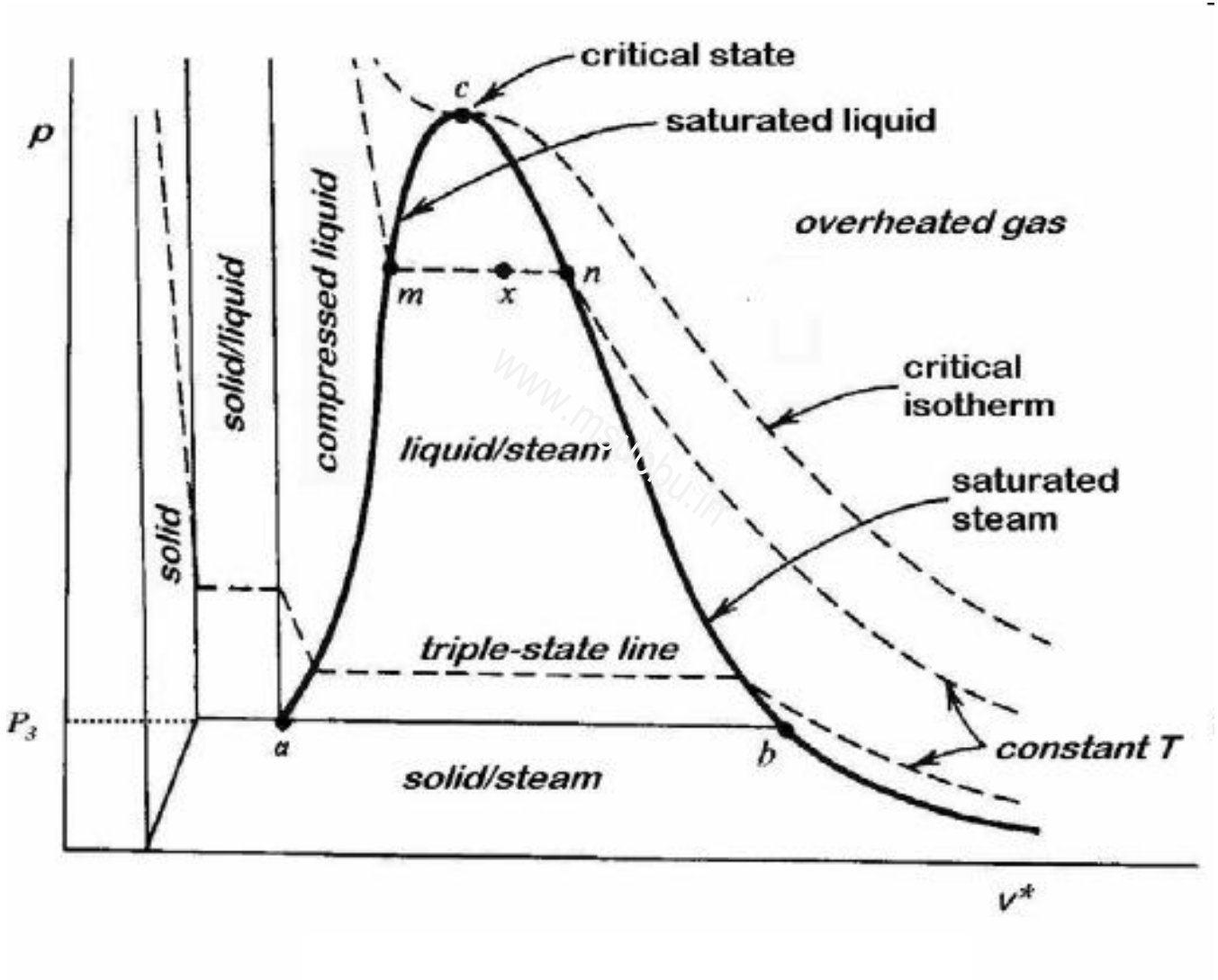
Critical point: P= 220.64 x 10^5 N/m2; T = 374^{o}C

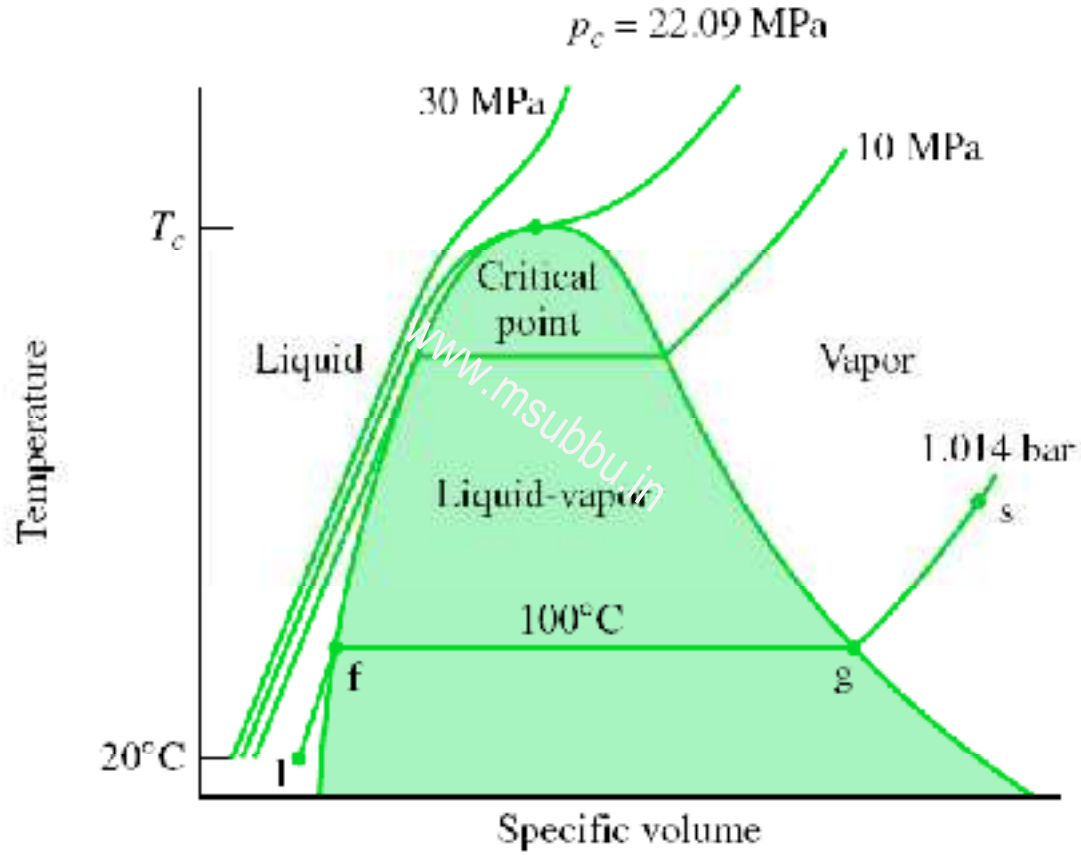
Normal boiling point: 100^{o}C; Normal freezing point: 0^{o}C (1 atm)

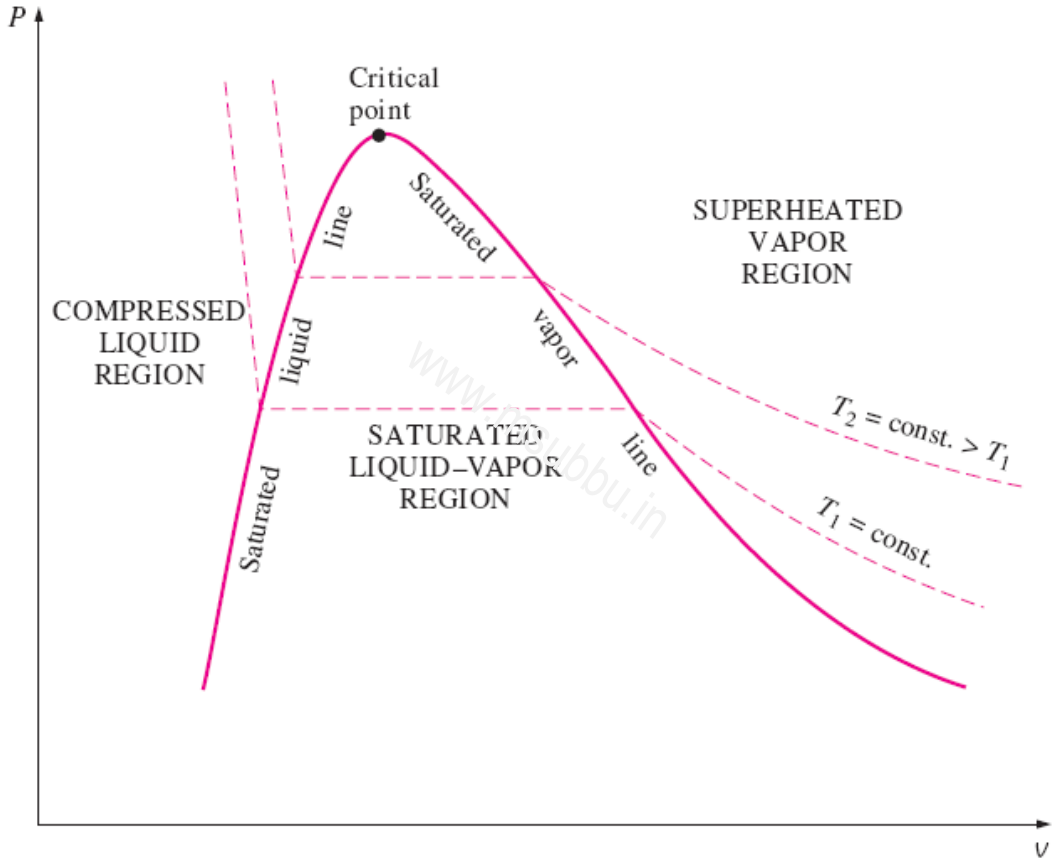

P
Liquid
B
C
A
T
K
D
P_T
Vapor
Solid
T_T
T

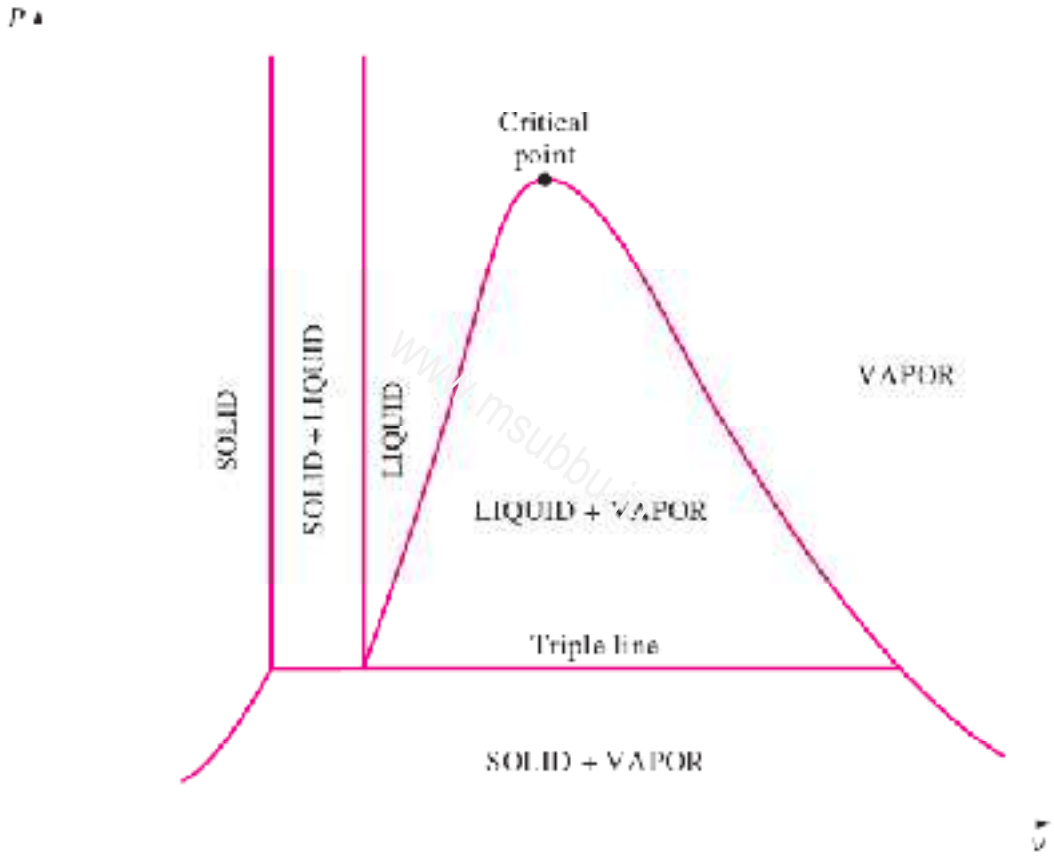

Critical
point
Liquid
a″ b″ c″
Melting
Vaporization
a b c
Solid
Vapor
Triple point
Sublimation
a′ b′ c′
Pressure
Temperature

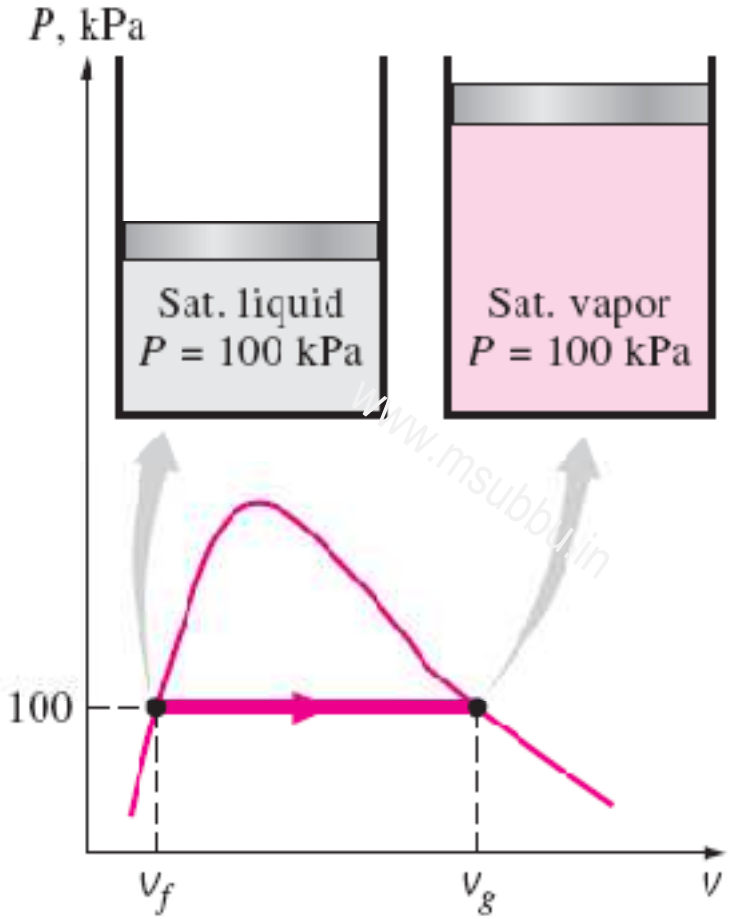

P
Substances
that expand
on freezing
Substances
that contract
on freezing
Critical
point
Melting
Melting
LIQUID
Vaporization
SOLID
Triple point
VAPOR
Sublimation
T


critical state
saturated liquid
overheated gas
critical
isotherm
saturated
steam
constant T
p
c
m
x
n
solid
solid/liquid
compressed liquid
liquid/steam
triple-state line
P_3
a
b
solid/steam
v^*

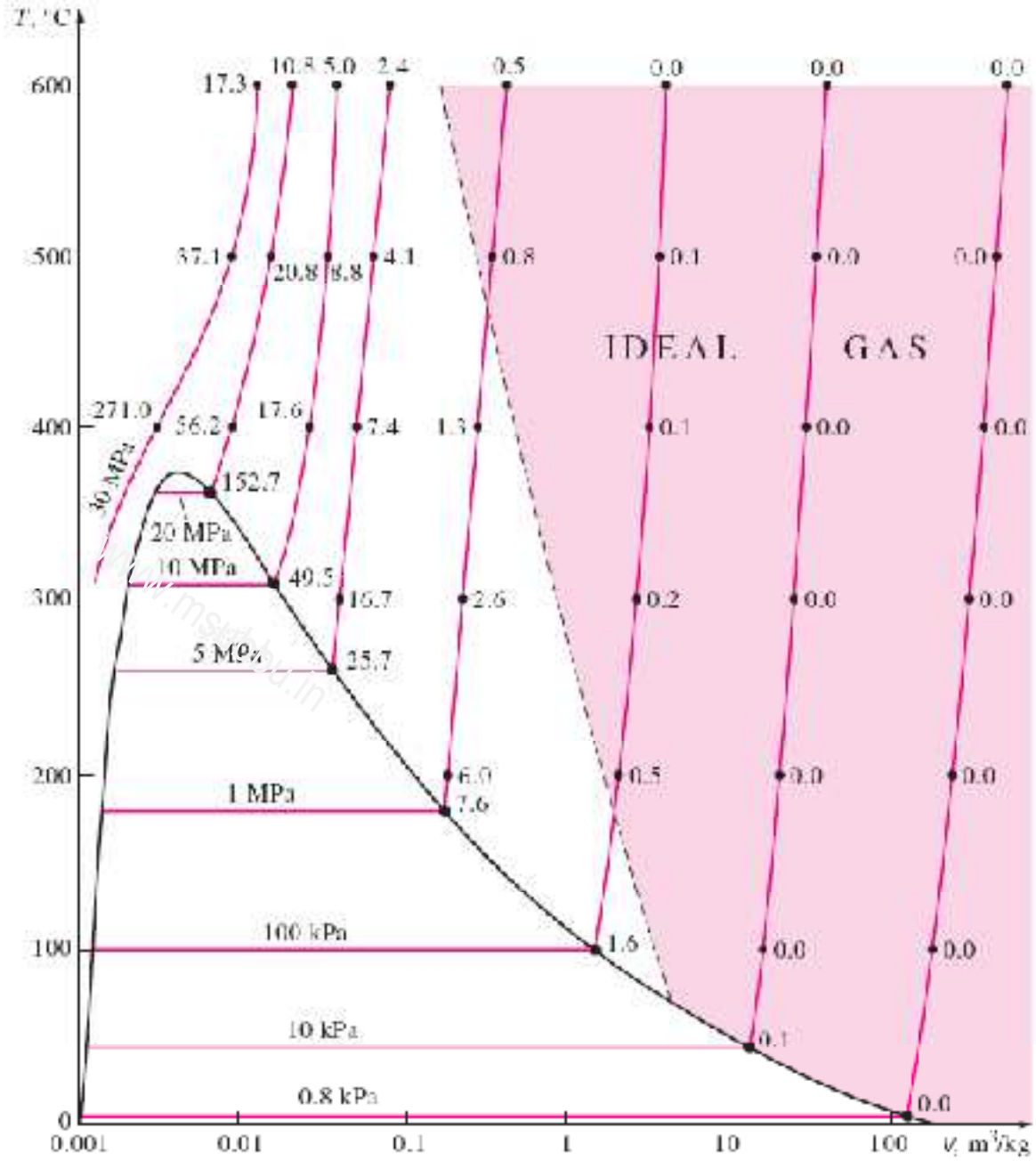



P
Critical point
Saturated liquid line
Saturated vapor line
SUPERHEATED VAPOR REGION
COMPRESSED LIQUID REGION
SATURATED LIQUID–VAPOR REGION
T_2 = const. > T_1
T_1 = const.
v

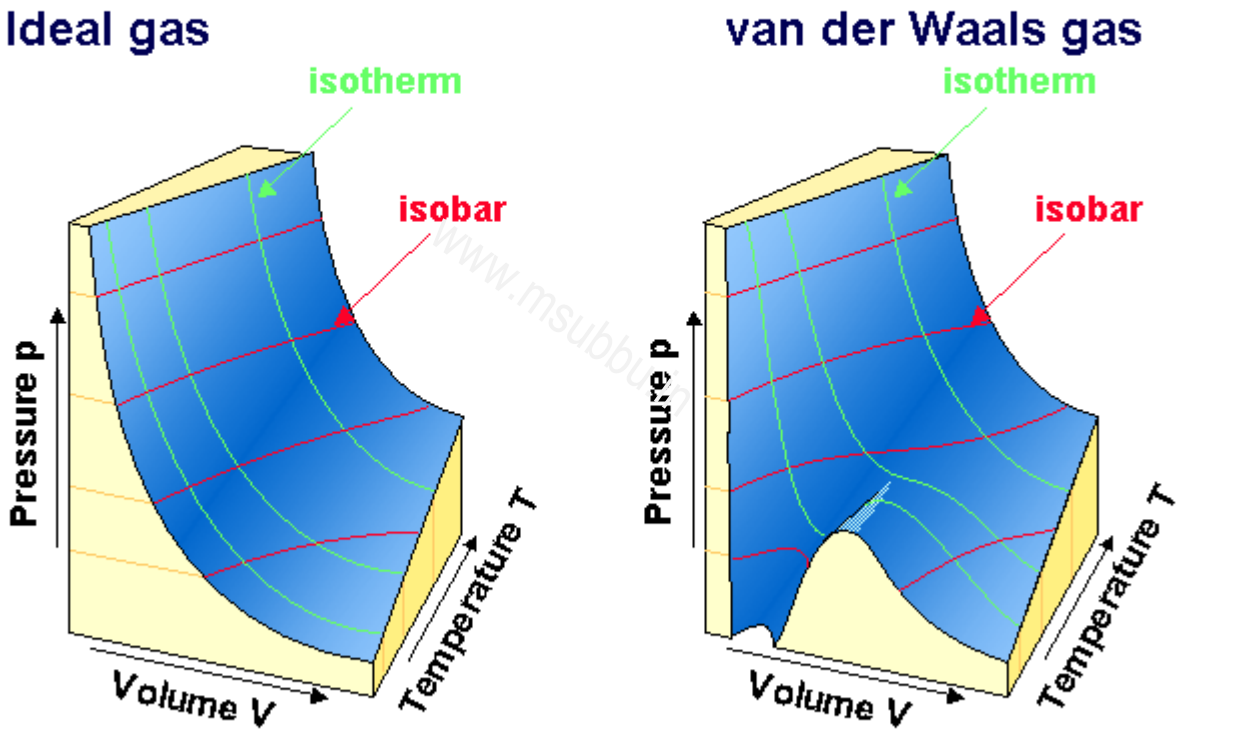

P
Critical point
SOLID
SOLID + LIQUID
LIQUID
VAPOR
LIQUID + VAPOR
Triple line
SOLID + VAPOR
T

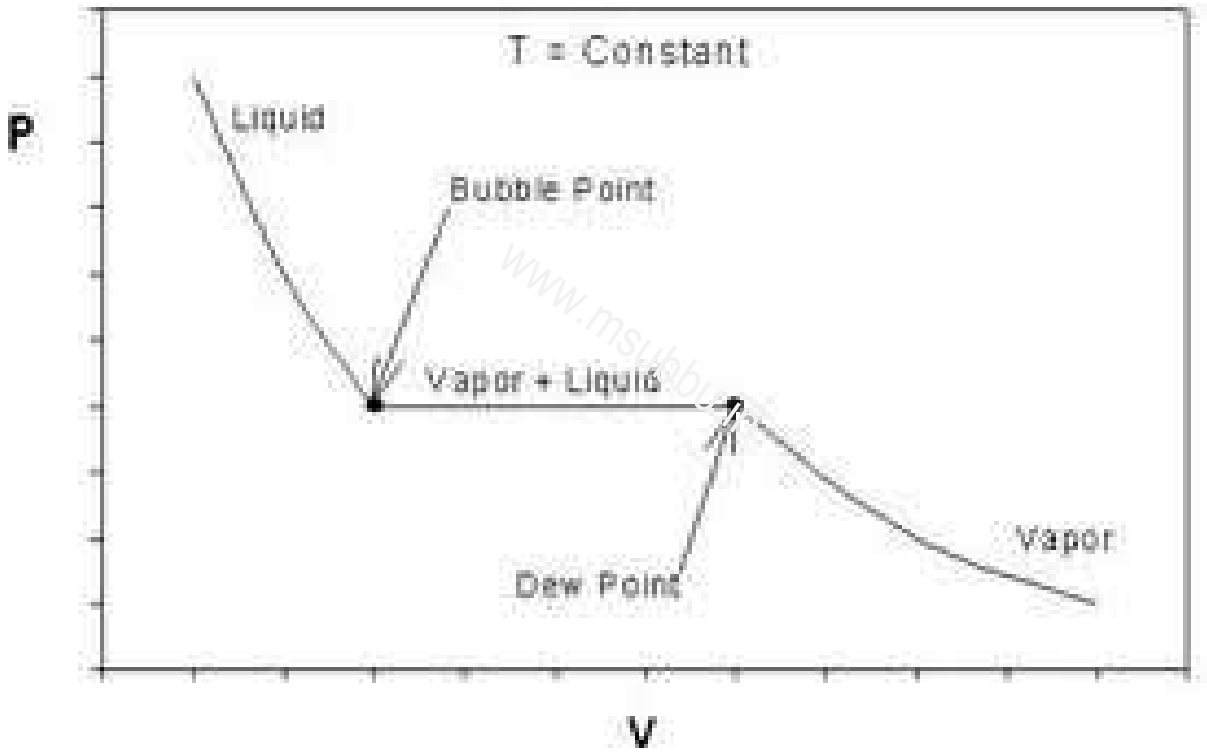

P, kPa
Sat. liquid
P = 100 kPa
Sat. vapor
P = 100 kPa
100
v_f
v_g
v

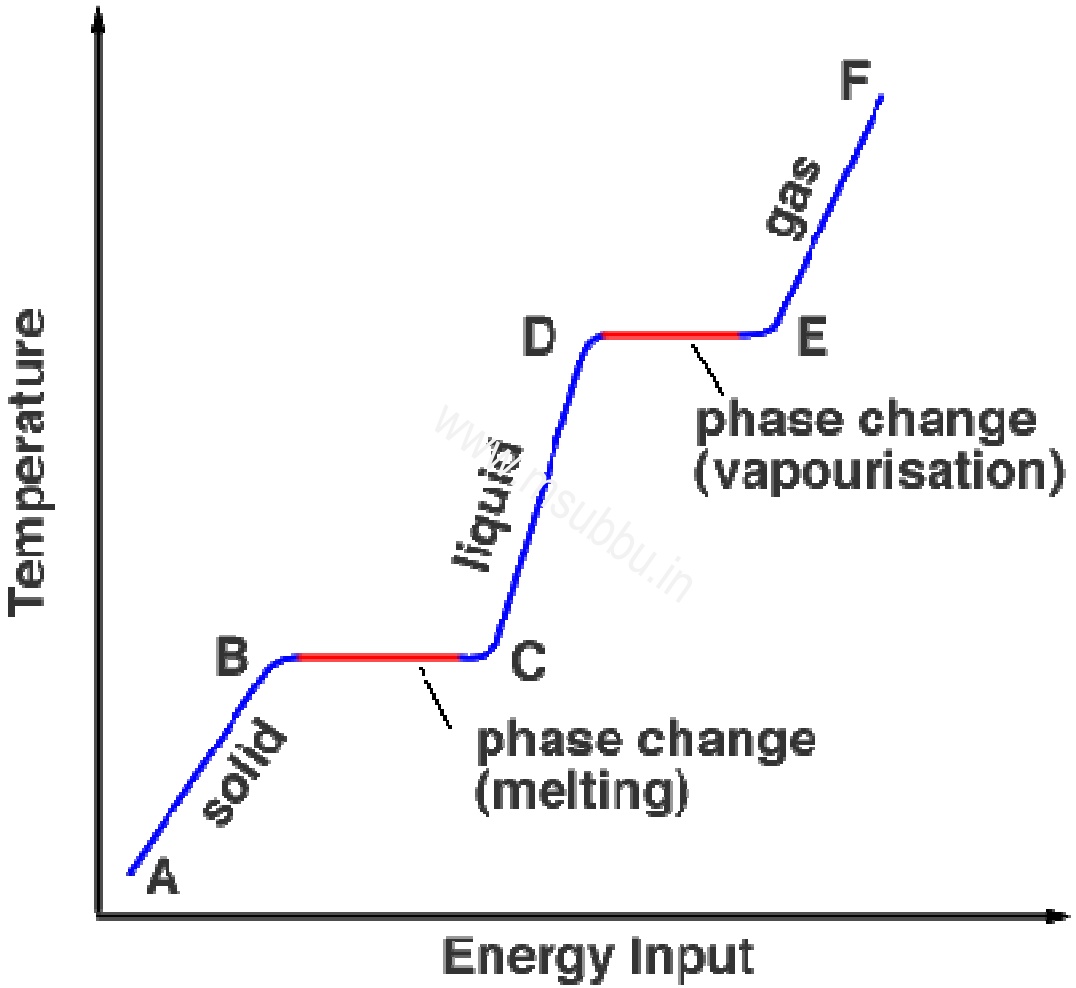
Percentage of error
$([|v_{table} - v_{ideal}|/v_{table}] \times 100)$
involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with less than 1 percent error.



Comparison of ideal and van der Waals gas




T = Constant
P
Liquid
Bubble Point
Vapor + Liquid
Vapor
Dew Point
V


Temperature
Energy Input
A
B
C
D
E
F
solid
liquid
gas
phase change
(melting)
phase change
(vapourisation)

van der Waals Equation

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

- The parameter **b** is related to the size of each molecule. The volume that the molecules have to move around in is not just the volume of the container **V**, but is reduced to (**V - b**).

- The parameter **a** is related to intermolecular attractive force between the molecules, and 1**/V** is the density of molecules. The net effect of the intermolecular attractive force is to reduce the pressure for a given volume and temperature.

- When the density of the gas is low (i.e., when 1**/V** is small and **b** is small compared to **V**) the van der Waals equation reduces to that of the ideal gas law.

van der Waals Constants

Substance	**a** ($J \cdot m^3/mole^2$)	**b** ($m^3/mole$)	**P_c** (MPa)	**T_c** (K)
Air	1.1358	3.64×10^{-5}	3.77	133
Carbon Dioxide (CO_2)	1.3643	4.27×10^{-5}	7.39	304.2
Nitrogen (N_2)	1.1361	3.85×10^{-5}	3.39	126.2
Hydrogen (H_2)	1.0247	2.65×10^{-5}	1.30	33.2
Water (H_2O)	1.5507	3.04×10^{-5}	22.09	647.3
Ammonia (NH_3)	1.4233	3.73×10^{-5}	11.28	406
Helium (He)	1.00341	2.34×10^{-5}	0.23	5.2
Freon (CCl_2F_2)	1.0780	9.98×10^{-5}	4.12	385

Observe that inert gases like Helium have a low value of **a** as one would expect since such gases do not interact very strongly, and that large molecules like Freon have large values of **b**.

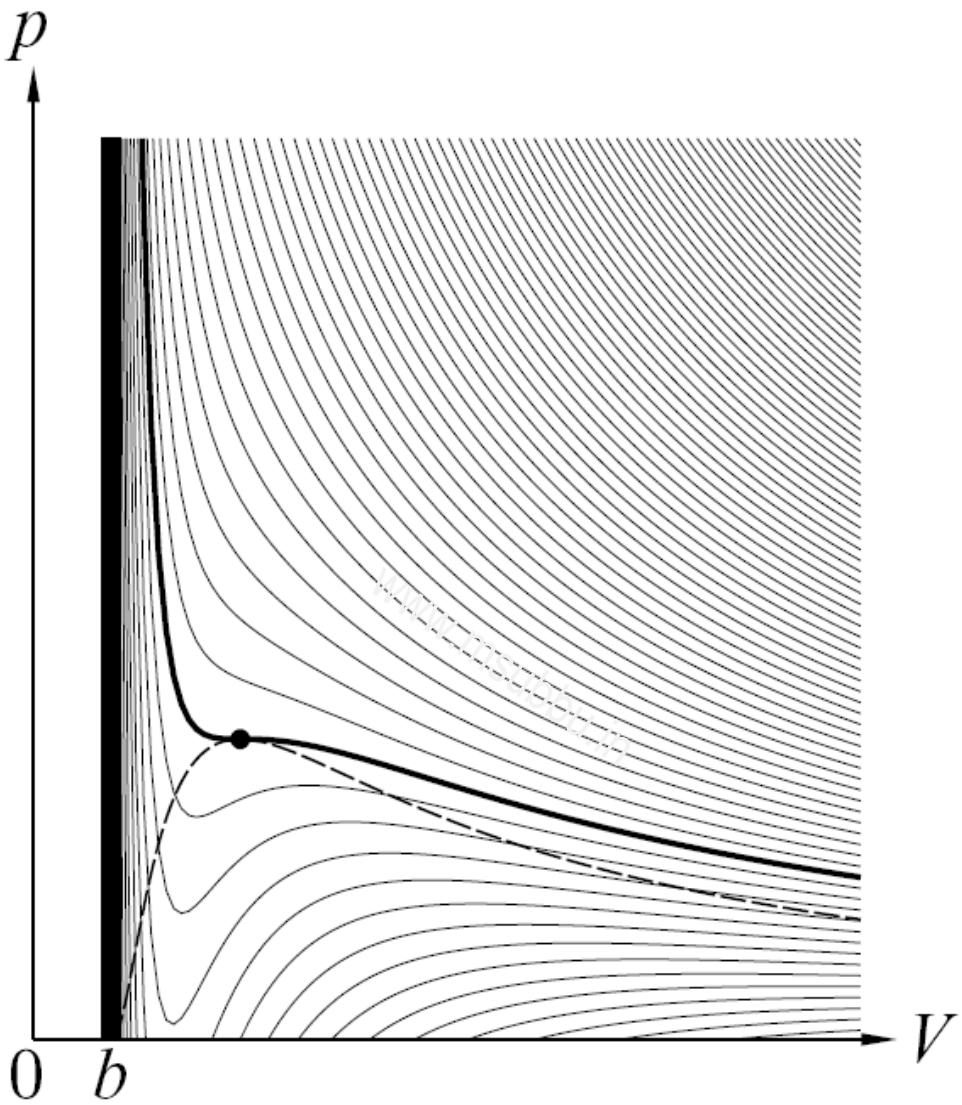
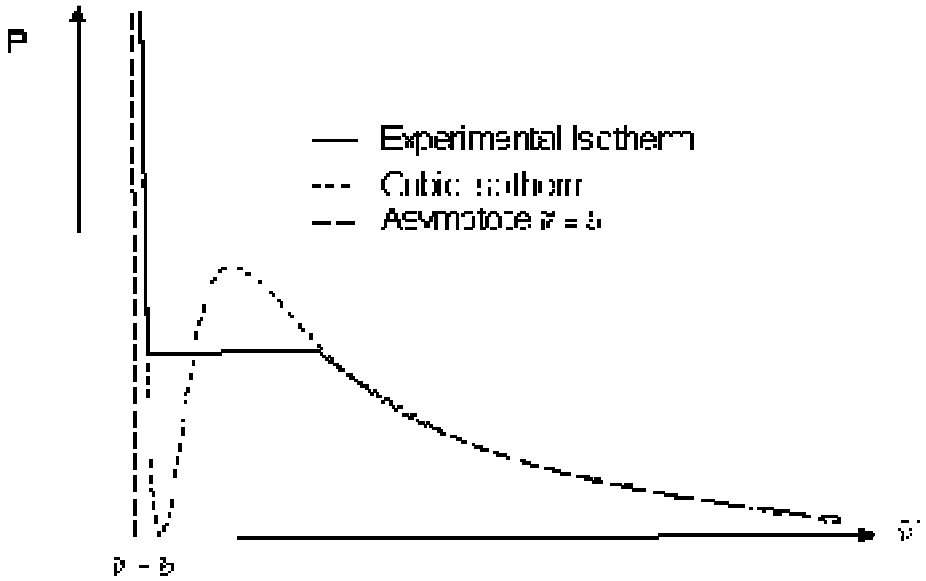
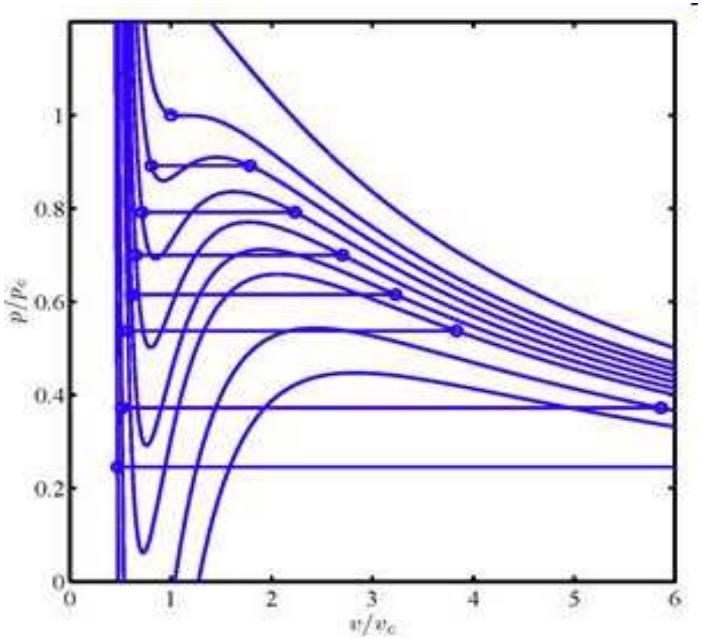
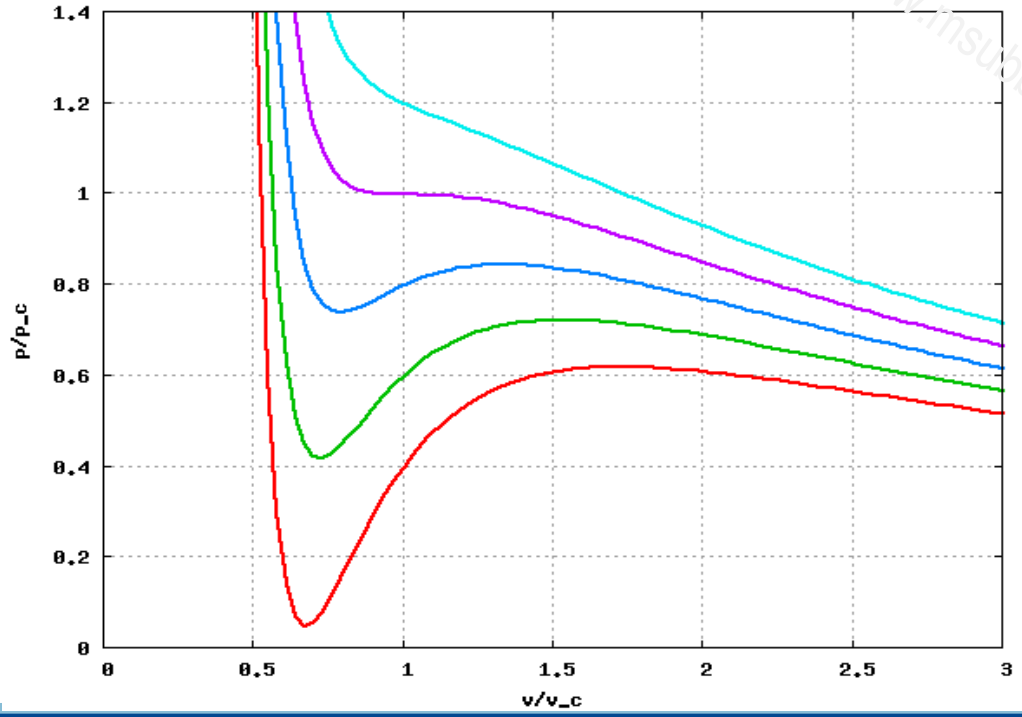
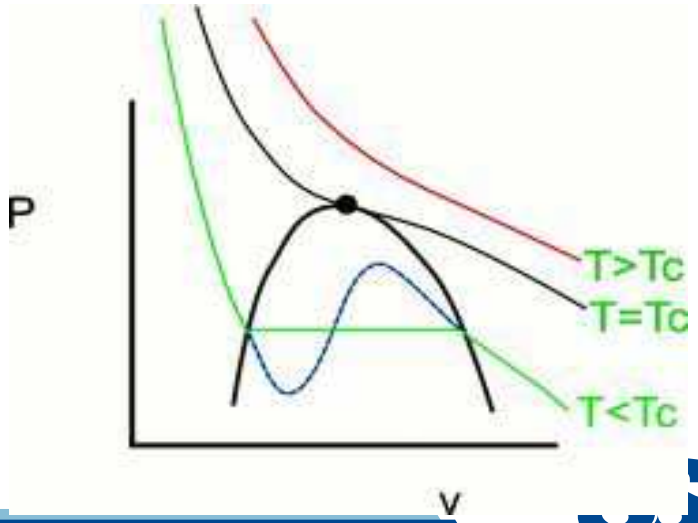


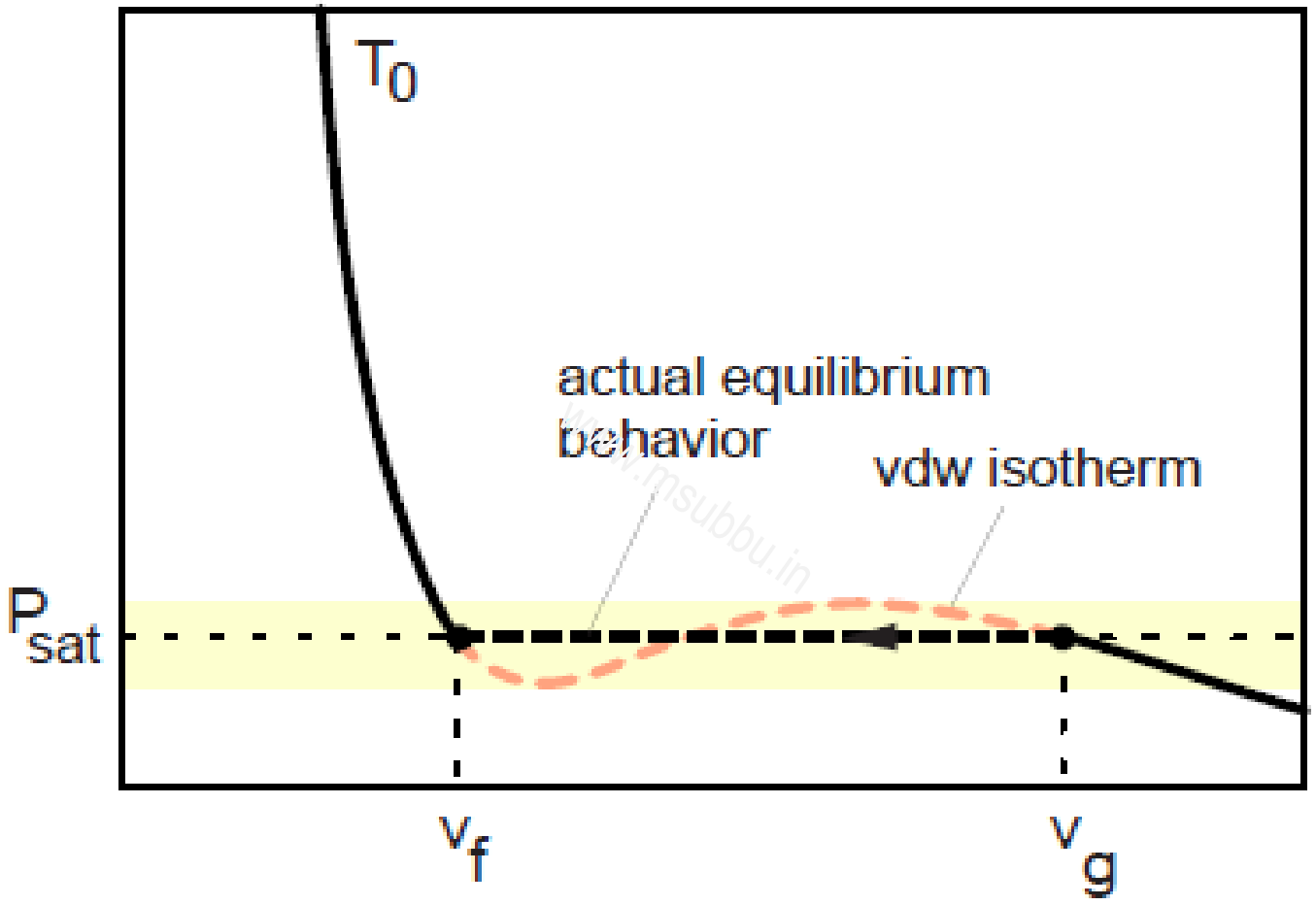
Fig. 26.2 Isotherms of the van der Waals gas. Isotherms towards to the top right of the graph correspond to higher temperatures. The dashed line shows the region in which liquid and vapour are in equilibrium (see the end of Section 26.1). The thick line is the critical isotherm and the dot marks the critical point.



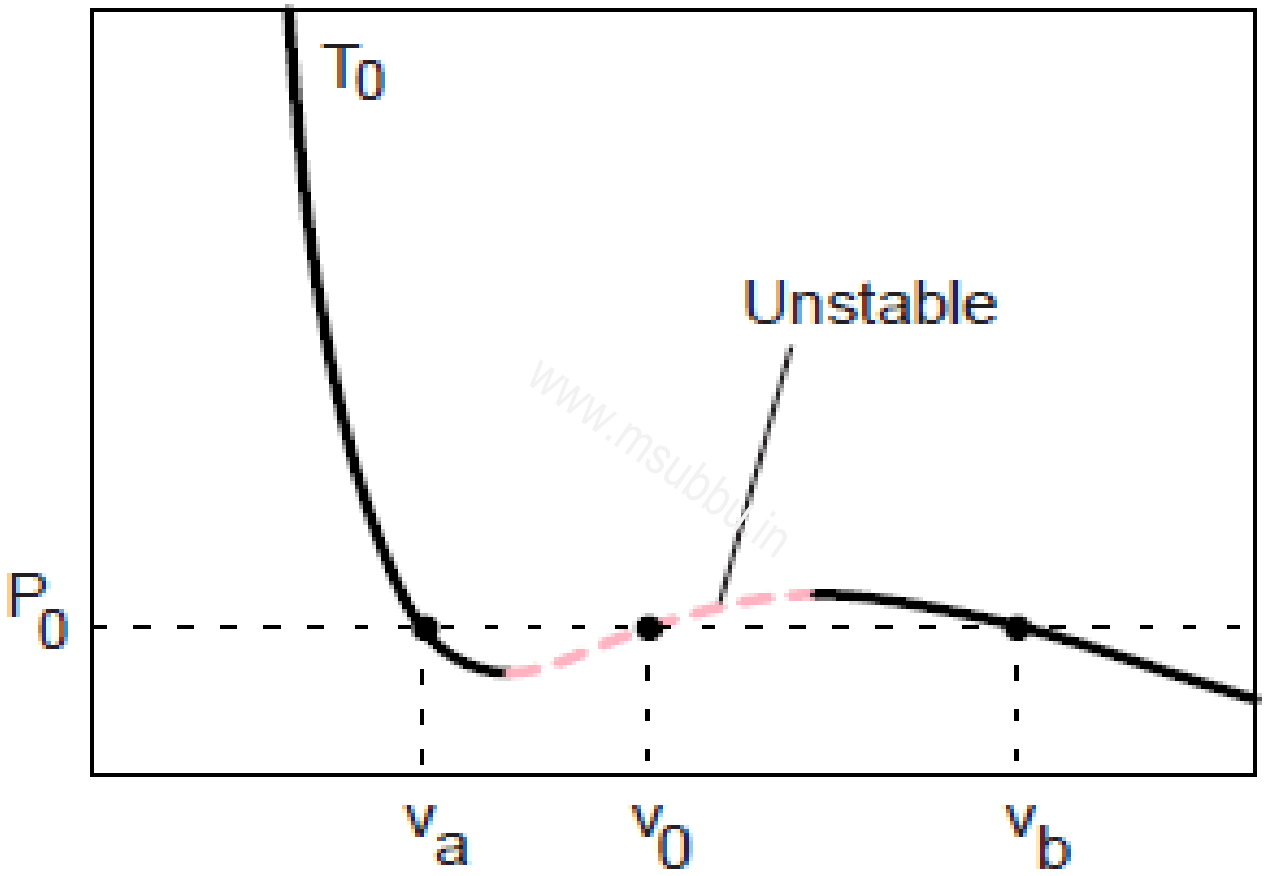








Comparison of actual behavior during isothermal compression to prediction of van der Waals equation.



An isotherm of the van der Waals equation for T < Tc.

van der Waals Equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{2.1}$$

where P = Pressure of the fluid
V = Volume of the container for containing one mole the fluid
a = correction term for pressure to account for the intermolecular forces of attraction
b = correction term for volume to account for the volume of molecules
R = Universal gas constant
T = Absolute temperature.

Eqn.(2.1) can be written as

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{2.2}$$

At the critical conditions (T_c, P_c, V_c)

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \tag{2.3a}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \tag{2.3b}$$

Taking derivative of Eqn.(2.2) with respect to V at constant T, i.e.,

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} \tag{2.4}$$

Using Eqn.(2.3a), Eqn.(2.4) becomes,

$$\frac{-RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0 \tag{2.5}$$

Taking second derivative of Eqn.(2.2) with respect to V at constant T and using using Eqn.(2.3b)

$$\frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0 \tag{2.6}$$

From Eqn.(2.5),

$$\frac{2a}{V_c^3} = \frac{RT_c}{(V_c - b)^2} \tag{2.7}$$

From Eqn.(2.6),

$$\frac{6a}{V_c^4} = \frac{2RT_c}{(V_c - b)^3} \tag{2.8}$$

Using Eqns.(2.7) and (2.8), we get

$$b = \frac{V_c}{3} \tag{2.9}$$

Substituting for b from Eqn.(2.9) in (2.5)

$$\frac{-RT_c}{\left(V_c - \frac{V_c}{3}\right)^2} + \frac{2a}{V_c^3} = 0$$

i.e.,

$$\frac{RT_c}{(4/9)V_c^2} = \frac{2a}{V_c^3}$$

giving,

$$a = \frac{9}{8} RT_c V_c \tag{2.10}$$

Substituting for a and b from Eqns.(2.10) and (2.9) in Eqn.(2.2), and at critical conditions,

$$\begin{aligned} P_c &= \frac{RT_c}{V_c - V_c/3} - \frac{9/8 RT_c V_c}{V_c^2} \\ &= \frac{3}{2}\frac{RT_c}{V_c} - \frac{9}{8}\frac{RT_c}{V_c} \end{aligned}$$

i.e.,

$$P_c = \frac{3}{8}\frac{RT_c}{P_c}$$

giving,

$$V_c = \frac{3}{8}\frac{RT_c}{P_c} \tag{2.11}$$

Using Eqn.(2.11) in Eqns.(2.9) and (2.10), we get

$$\boxed{a = \frac{27}{64}\frac{R^2T_c^2}{P_c}} \tag{2.12}$$

and

$$\boxed{b = \frac{RT_c}{8P_c}} \tag{2.13}$$

2.1.2 Derivation for a and b in another way

van der Waals equation is given as

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

Expanding the equation and rearranging, we get the following cubic equation for V:

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P} - \frac{ab}{P} = 0 \tag{2.14}$$

Being a cubic equation, it has three roots for V. At $T = T_c$, all the three roots merge into one, i.e., V_c. i.e.,

$$(V - V_c)^3 = 0$$

Expanding the above,

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \tag{2.15}$$

Comparing the coefficients of Eqns.(2.14) and (2.15), at T_c and P_c, we get

$$3V_c = b + \frac{RT_c}{P_c} \tag{2.16}$$

$$3V_c^2 = \frac{a}{P_c} \tag{2.17}$$

$$V_c^3 = \frac{ab}{P_c} \tag{2.18}$$

Eliminating P_c from Eqns.(2.17) and (2.18), we get

$$b = \frac{V_c}{3} \tag{2.19}$$

Substituting for V_c using Eqn.(2.19), in Eqn.(2.16), we get,

$$9b = b + \frac{RT_c}{P_c}$$

i.e.,

$$\boxed{b = \frac{RT_c}{8P_c}} \tag{2.20}$$

Substituting for V_c using Eqn.(2.19), in Eqn.(2.17), we get

$$3 \times (3b)^2 = \frac{a}{P_c}$$

i.e.,

$$27b^2 = \frac{a}{P_c} \tag{2.21}$$

Using Eqn.(2.20) in above equation, we get,

$$\boxed{a = \frac{27}{64}\frac{RT_c^2}{P_c}} \tag{2.22}$$

Redlich-Kwong Equation

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)}$$

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c}$$

$$b = 0.08664\frac{RT_c}{P_c}$$

Berthelot Equation

$$P = \frac{RT}{V - b} - \frac{a}{TV^2}$$

$$a = \frac{27}{64}\frac{R^2 T_c^3}{P_c}$$

$$b = \frac{RT_c}{8P_c}$$

Dieterici Equation

$$P = \frac{RT}{V - b} \exp\left(\frac{-a}{RTV}\right)$$

$$a = \frac{4R^2T_c^2}{P_c \exp(2)}$$

$$b = \frac{RT_c}{P_c \exp(2)}$$

26.2 The Dieterici equation

The van der Waals equation of state can be written in the form

$$p = p_{\text{repulsive}} + p_{\text{attractive}}, \tag{26.31}$$

where the first term is a repulsive hard sphere interaction

$$p_{\text{repulsive}} = \frac{RT}{V - b}, \tag{26.32}$$

which is an ideal-gas-like term but with the denominator being the volume available to gas molecules, namely that of the container V minus

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that of the molecules, b. The second term is the attractive interaction

$$p_{\text{attractive}} = -\frac{a}{V^2}. \tag{26.33}$$

There have been other attempts to model non-ideal gases. In the **Berthelot equation**, the attractive force is made temperature-dependent by writing

$$p_{\text{attractive}} = -\frac{a}{TV^2}. \tag{26.34}$$

Another approach is due to Dieterici,[2] who in 1899 proposed an alternative equation of state in which he wrote that

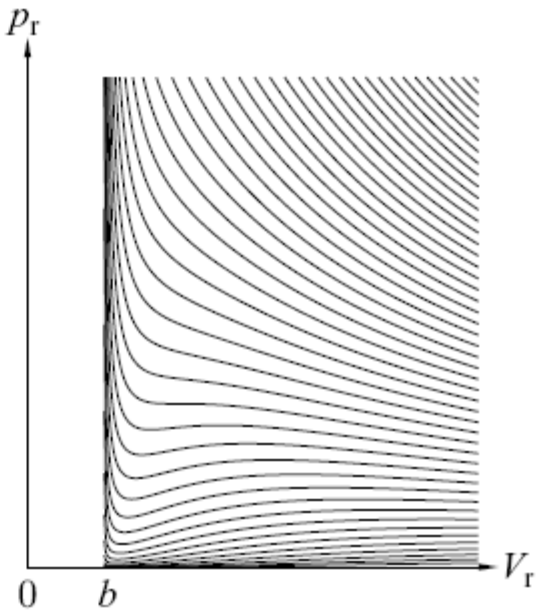
$$p = p_{\text{repulsive}} \exp\left(-\frac{a}{RTV}\right), \tag{26.35}$$

and using eqn 26.32 this leads to

$$\boxed{p(V_{\text{m}} - b) = RT \exp\left(-\frac{a}{RTV_{\text{m}}}\right),} \tag{26.36}$$

which is the **Dieterici equation**, here written in terms of the molar volume. The constant a is, again, a parameter which controls the strength of attractive interactions. Isotherms of the Dieterici equation of state are shown in Fig. 26.7; they are similar to the ones for the van der Waals gas (Fig. 26.2), showing a very sudden increase in pressure as V approaches b.

[2] Conrad Dieterici (1858–1929)



The critical point can be identified for this model by evaluating

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \left(\frac{\partial p}{\partial V}\right)_T = 0, \tag{26.37}$$

and this yields (after a little algebra)

$$T_c = \frac{a}{4Rb}, \quad p_c = \frac{a}{4e^2 b^2}, \quad V_c = 2b, \tag{26.38}$$

for the critical temperature, pressure and volume, and hence

$$\frac{p_c V_c}{RT_c} = \frac{2}{e^2} = 0.271. \tag{26.39}$$

26.3 Virial expansion

Another method to model real gases is to take the ideal gas equation and modify it using a power series in $1/V_\mathrm{m}$ (where V_m is the molar volume). This leads to the following **virial expansion**:

$$\frac{pV_\mathrm{m}}{RT} = 1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \cdots \tag{26.40}$$

In this equation, the parameters B, C, etc. are called **virial coefficients** and can be made to be temperature dependent (so that we will denote them by $B(T)$ and $C(T)$). The temperature at which the virial coefficient $B(T)$ goes to zero is called the **Boyle temperature** T_B since it is the temperature at which Boyle's law is approximately obeyed (neglecting the higher–order virial coefficients), as shown in Fig. 26.8.

26.4 The law of corresponding states

For different substances, the size of the molecules (which controls b in the van der Waals model) and the strength of the intermolecular interactions (which controls a in the van der Waals model) will vary, and hence their phase diagrams will be different. For example, the critical temperatures and pressures for different gases are different. However, the phase diagram of substances should be the same when plotted in **reduced coordinates**, which can be obtained by dividing a quantity by its value at the critical point. Hence, if we replace the quantities p, V, T by their reduced coordinates $\tilde{p}, \tilde{V}, \tilde{T}$ defined by

$$\tilde{p} = \frac{p}{p_c}, \qquad \tilde{V} = \frac{V}{V_c}, \qquad \tilde{T} = \frac{T}{T_c}, \tag{26.61}$$

then phase diagrams of materials which are not wholly different from one another should lie on top of each other. This is called the **law of corresponding states**.

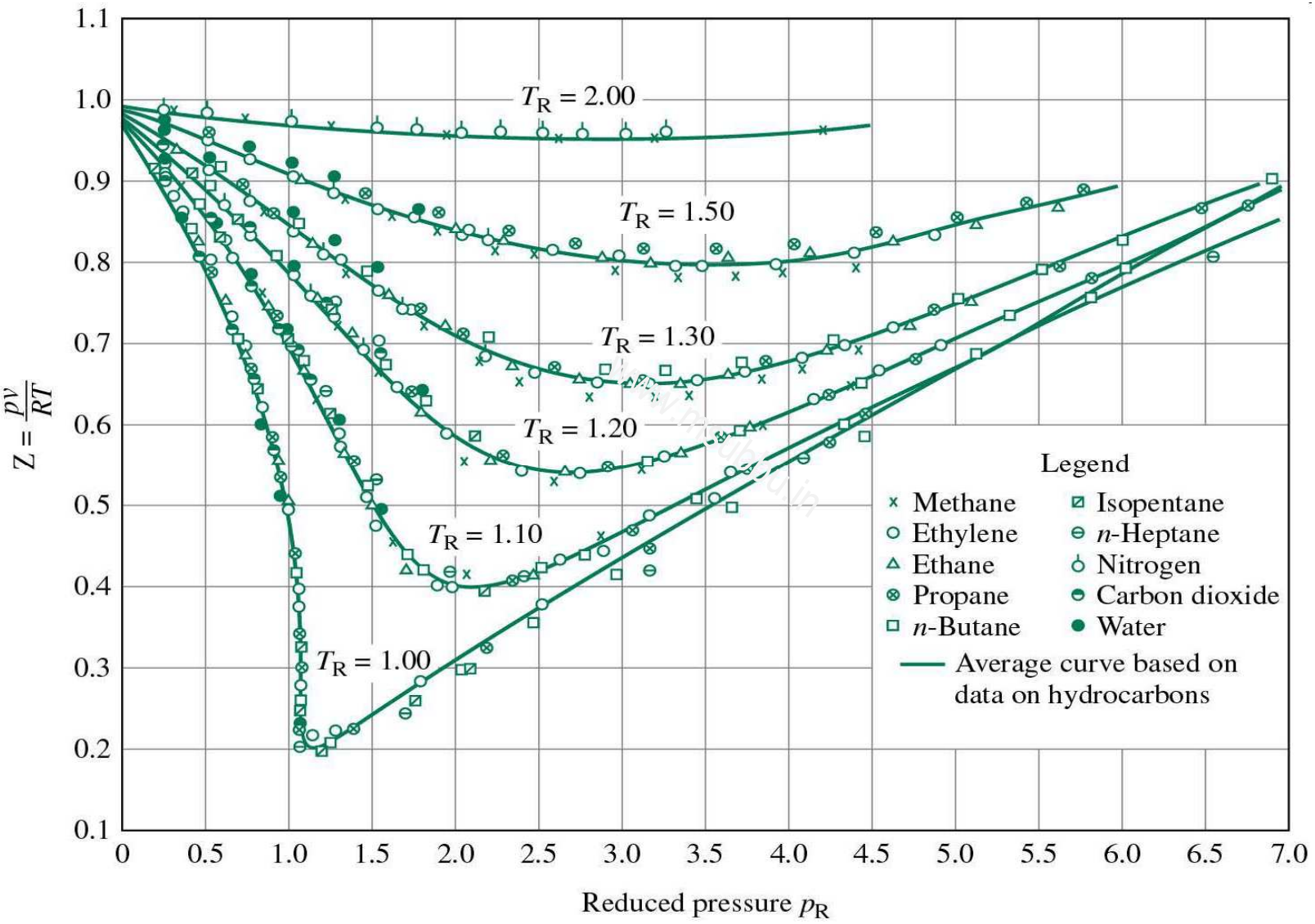
Virial Equation

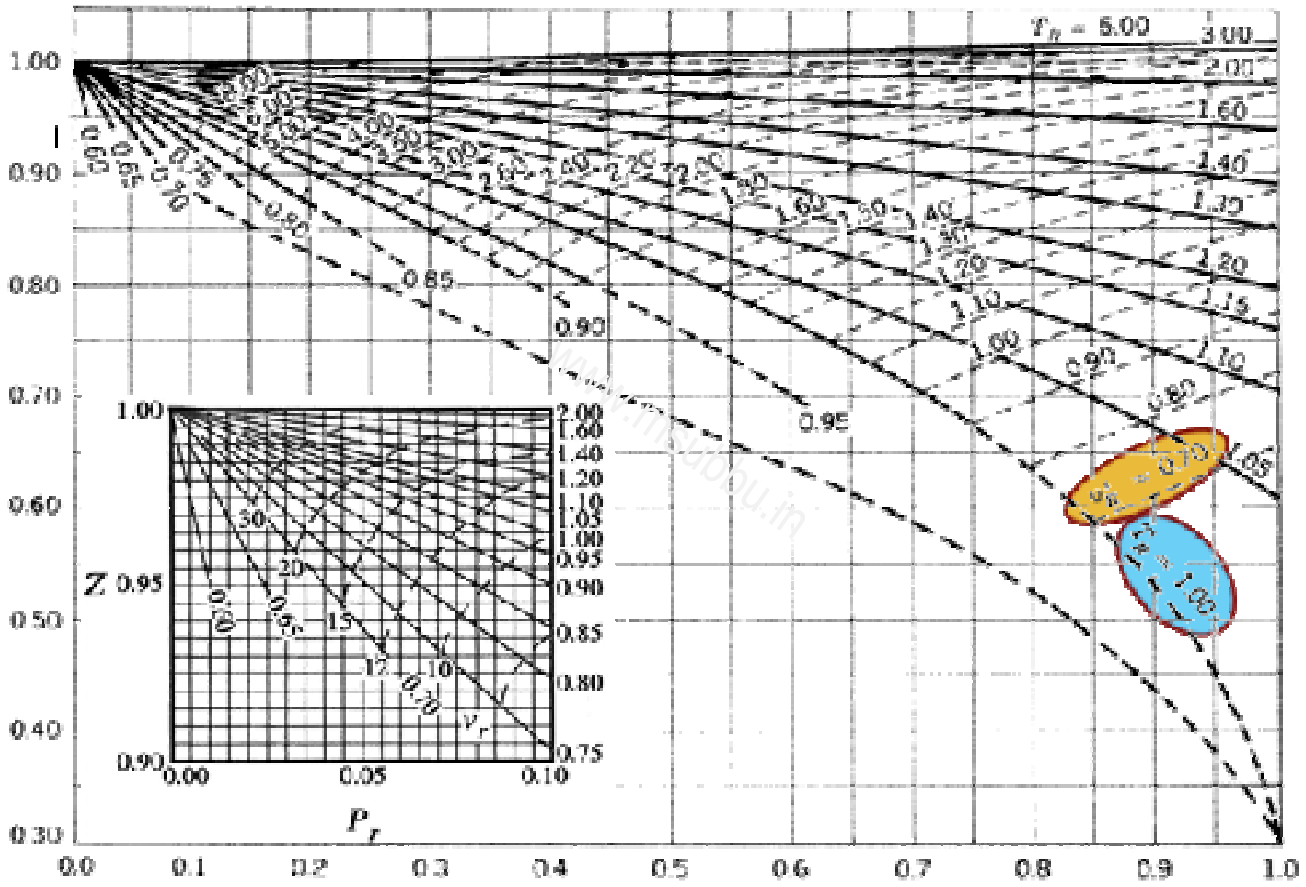
$$z = 1 + B'P + C'P^2 + D'P^3 + \cdots$$

or

$$z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots$$

Corresponding State Principle


1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
$Z = \frac{pv}{RT}$
$T_R = 2.00$
$T_R = 1.50$
$T_R = 1.30$
$T_R = 1.20$
$T_R = 1.10$
$T_R = 1.00$
Legend
Methane
Ethylene
Ethane
Propane
n-Butane
Isopentane
n-Heptane
Nitrogen
Carbon dioxide
Water
Average curve based on data on hydrocarbons
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
Reduced pressure p_R


1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
T_r = 5.00
3.00
2.00
1.60
1.40
1.30
1.20
1.15
1.10
1.05
1.03
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
Z 0.95
0.90
1.00
0.95
0.90
0.85
0.80
0.75
2.00
1.60
1.40
1.20
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.00
0.05
0.10
P_r
50
30
20
15
12
10
v_r
v_r = 0.70
v_r = 1.00

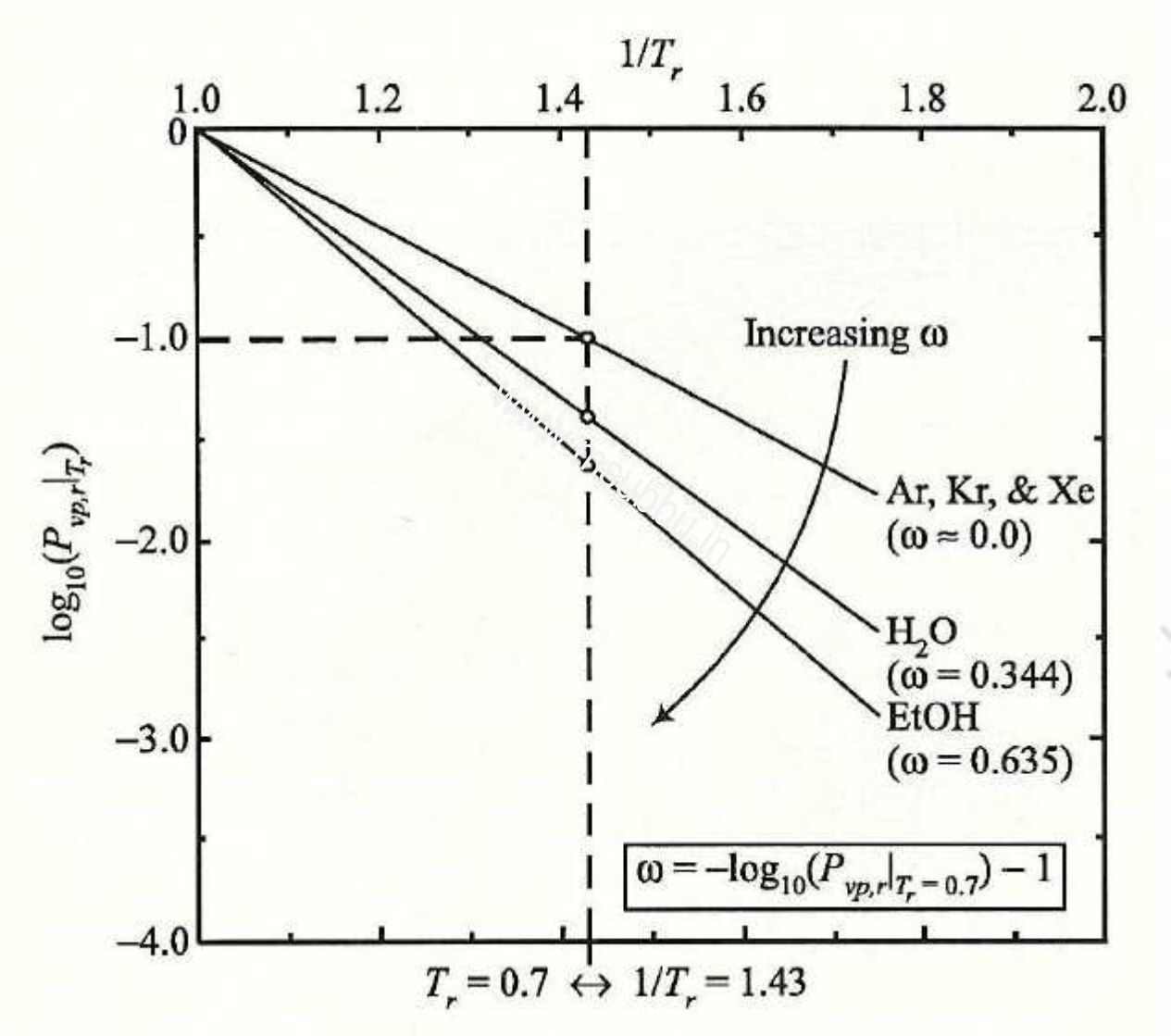
$$Z = f(T_r, P_r)$$

To improve the accuracy of property predictions, Pitzer and coworkers introduced the acentric factor ω as a third correlating parameter.

$$Z = Z^{(0)}(T_r, P_r) + \omega Z^{(1)}(T_r, P_r)$$

$$\omega = -\log_{10} P_r^{\text{sat}}|_{T_r=0.7} - 1$$

$$\omega = -\log_{10} P_r^{\text{sat}}|_{T_r=0.7} - 1$$



The Lee/Kesler Generalized Correlation for the Compressibilty Factor

Z°									
Tr ↓	Pr →	0.01	0.05	0.10	0.20	0.40	0.60	0.80	1.00
0.30		0.0029	0.0145	0.0290	0.0579	0.1158	0.1737	0.2315	0.2892
0.35		0.0026	0.0130	0.0261	0.0522	0.1043	0.1564	0.2084	0.2604
0.40		0.0024	0.0119	0.0239	0.0477	0.0953	0.1429	0.1904	0.2379
0.45		0.0022	0.0110	0.0221	0.0442	0.0882	0.1322	0.1762	0.2200
0.50		0.0021	0.0103	0.0207	0.0413	0.0825	0.1236	0.1647	0.2056
0.55		0.9804	0.0098	0.0195	0.0390	0.0778	0.1166	0.1553	0.1939
0.60		0.9849	0.0093	0.0186	0.0371	0.0741	0.1109	0.1476	0.1842
0.65		0.9881	0.9377	0.0178	0.0356	0.0710	0.1063	0.1415	0.1765
0.70		0.9904	0.9504	0.8958	0.0344	0.0687	0.1027	0.1366	0.1703
0.75		0.9922	0.9598	0.9165	0.0336	0.0670	0.1001	0.1330	0.1656
0.80		0.9935	0.9669	0.9319	0.8539	0.0661	0.0985	0.1307	0.1626
0.85		0.9946	0.9725	0.9436	0.8810	0.0661	0.0983	0.1301	0.1614
0.90		0.9954	0.9768	0.9528	0.9015	0.7800	0.1006	0.1321	0.1630
0.93		0.9959	0.9790	0.9573	0.9115	0.8059	0.6635	0.1359	0.1664

Steam Tables

Temp. °C T	Press. kPa, MPa P	Specific Volume, m³/kg: Sat. Liquid v_f	Specific Volume, m³/kg: Sat. Vapor v_g	Internal Energy, kJ/kg: Sat. Liquid u_f	Internal Energy, kJ/kg: Evap. u_{fg}	Internal Energy, kJ/kg: Sat. Vapor u_g	Enthalpy, kJ/kg: Sat. Liquid h_f	Enthalpy, kJ/kg: Evap. h_{fg}	Enthalpy, kJ/kg: Sat. Vapor h_g	Entropy, kJ/kg: Sat. Liquid s_f	Entropy, kJ/kg: Evap. s_{fg}
0.01 TP	0.6113	0.001000	206.132	0.00	2375.3	2375.3	0.00	2501.3	2501.3	0.0000	9.1562
5	0.8721	0.001000	147.118	20.97	2361.3	2382.2	20.98	2489.6	2510.5	0.0761	8.9496
10	1.2276	0.001000	106.377	41.99	2347.2	2389.2	41.99	2477.7	2519.7	0.1510	8.7498
15	1.7051	0.001001	77.925	62.98	2333.1	2396.0	62.98	2465.9	2528.9	0.2245	8.5569
20	2.3385	0.001002	57.790	83.94	2319.0	2402.9	83.94	2454.1	2538.1	0.2966	8.3706
25	3.1691	0.001003	43.359	104.86	2304.9	2409.8	104.87	2442.3	2547.2	0.3673	8.1905
30	4.2461	0.001004	32.893	125.77	2290.8	2416.6	125.77	2430.5	2556.2	0.4369	8.0164
35	5.6280	0.001006	25.216	146.65	2276.7	2423.4	146.66	2418.6	2565.3	0.5052	7.8478
40	7.3837	0.001008	19.523	167.53	2262.6	2430.1	167.54	2406.7	2574.3	0.5724	7.6845
75	38.578	0.001026	4.131	313.87	2162.0	2475.9	313.91	2321.4	2635.3	1.0154	6.6670
80	47.390	0.001029	3.407	334.84	2147.4	2482.2	334.88	2308.8	2643.7	1.0752	6.5369
85	57.834	0.001032	2.828	355.82	2132.6	2488.4	355.88	2296.0	2651.9	1.1342	6.4102
90	70.139	0.001036	2.361	376.82	2117.7	2494.5	376.90	2283.2	2660.1	1.1924	6.2866
95	84.554	0.001040	1.982	397.86	2102.7	2500.6	397.94	2270.2	2668.1	1.2500	6.1659
100	0.10135	0.001044	1.6729	418.91	2087.6	2506.5	419.02	2257.0	2676.0	1.3068	6.0480
340	14.586	0.001638	0.010797	1570.26	894.3	2464.5	1594.15	1027.9	2622.0	3.6593	1.6763
350	16.514	0.001740	0.008813	1641.81	776.6	2418.4	1670.54	893.4	2563.9	3.7776	1.4336
360	18.651	0.001892	0.006945	1725.19	626.3	2351.5	1760.48	720.5	2481.0	3.9146	1.1379
370	21.028	0.002213	0.004926	1843.84	384.7	2228.5	1890.37	441.8	2332.1	4.1104	0.6868
374.1 CP	22.089	0.003155	0.003155	2029.58	0	2029.6	2099.26	0	2099.3	4.4297	0

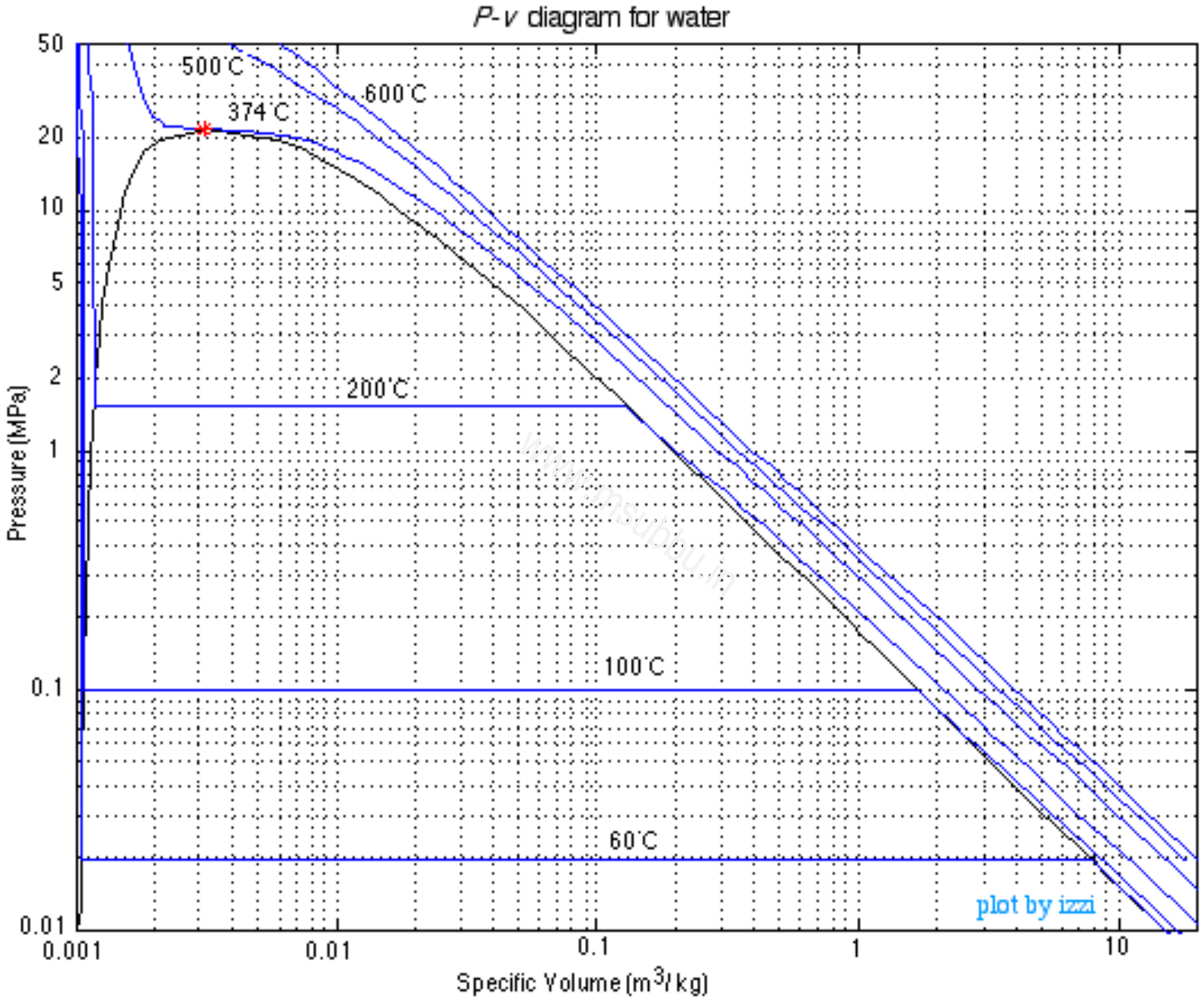
Single-phase tables

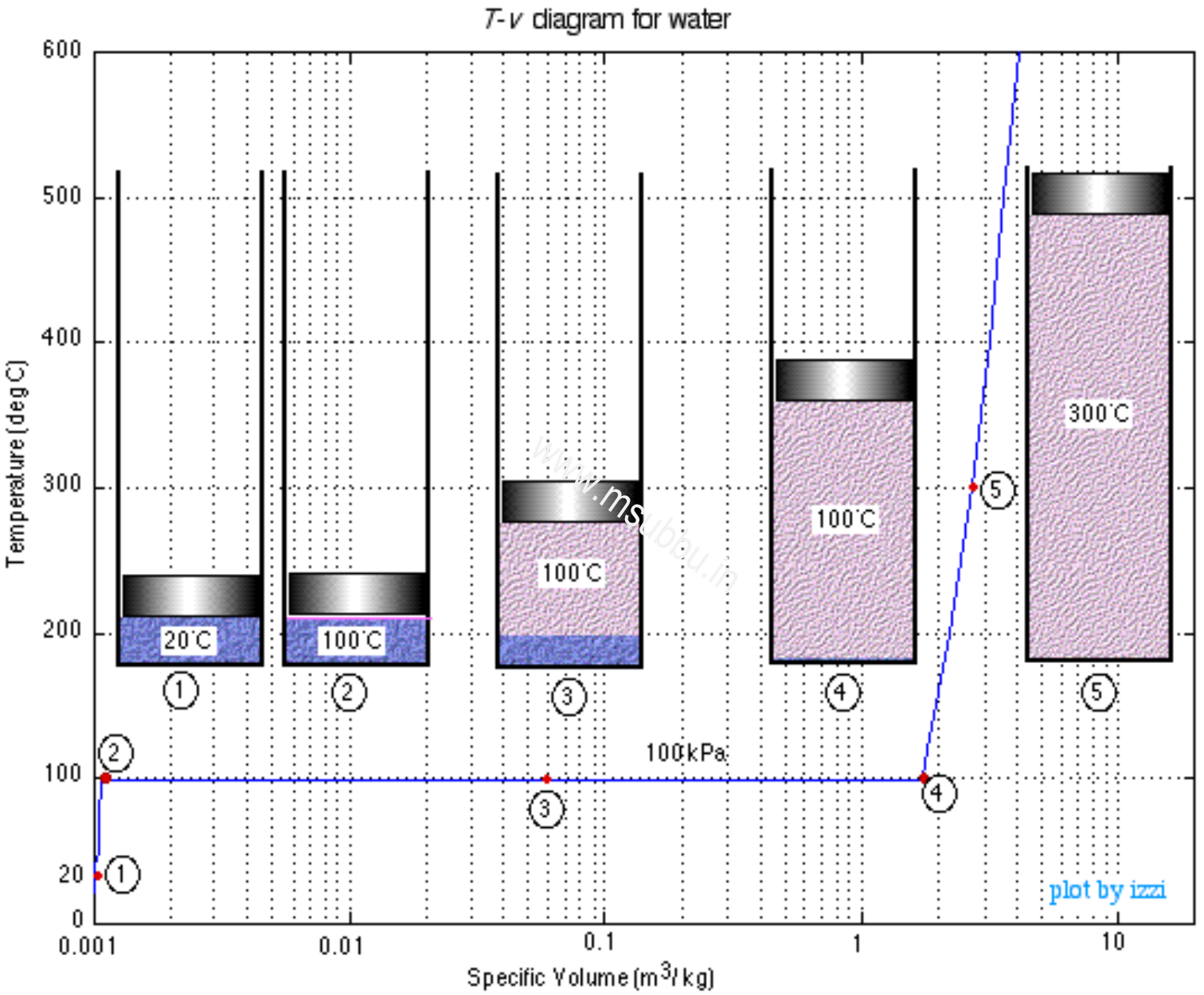
TABLE A.1.3SI *Superheated Vapor Water (SI Units)*

	P = 10 kPa (45.81)				P = 50 kPa (81.33)			
T	v	u	h	s	v	u	h	s
Sat.	14.674	2437.9	2584.6	8.1501	3.240	2483.8	2645.9	7.593
50	14.869	2443.9	2592.6	8.1749	—	—	—	—
100	17.196	2515.5	2687.5	8.4479	3.418	2511.6	2682.5	7.694
150	19.513	2587.9	2783.0	8.6881	3.889	2585.6	2780.1	7.940
200	21.825	2661.3	2879.5	8.9037	4.356	2659.8	2877.6	8.157
250	24.136	2736.0	2977.3	9.1002	4.821	2735.0	2976.0	8.355
300	26.445	2812.1	3076.5	9.2812	5.284	2811.3	3075.5	8.537

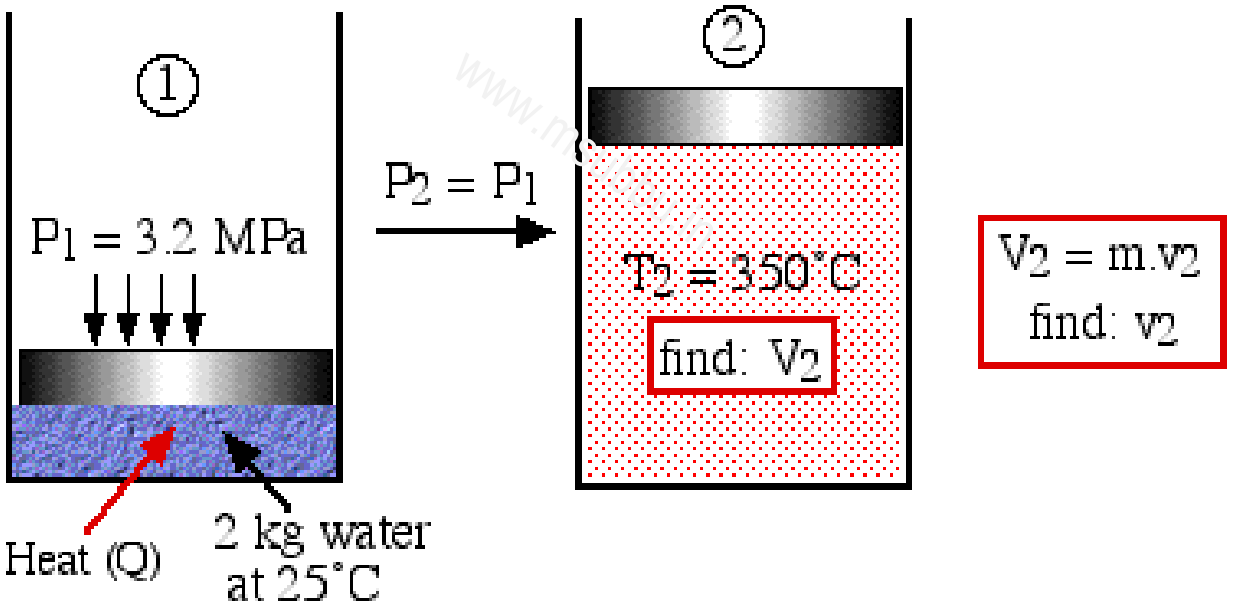
TABLE A.1.4SI *Compressed Liquid Water (SI Units)*

	P = 5.00 MPa (263.99)				P = 10.00,MPa (311.06)			
T	v	u	h	s	v	u	h	s
Sat.	.0012859	1147.78	1154.21	2.9201	.0014524	1393.00	1407.53	3.35
0	.0009977	0.03	5.02	0.0001	.0009952	0.10	10.05	0.00
20	.0009995	83.64	88.64	0.2955	.0009972	83.35	93.32	0.29
40	.0010056	166.93	171.95	0.5705	.0010034	166.33	176.36	0.56
60	.0010149	250.21	255.28	0.8284	.0010127	249.34	259.47	0.82
80	.0010268	333.69	338.83	1.0719	.0010245	332.56	342.81	1.06
100	.0010410	417.50	422.71	1.3030	.0010385	416.09	426.48	1.29


P-v diagram for water
500°C
600°C
374°C
200°C
100°C
60°C
Pressure (MPa)
50
20
10
5
2
1
0.1
0.01
0.001
0.01
0.1
1
10
Specific Volume (m3/kg)
plot by izzi

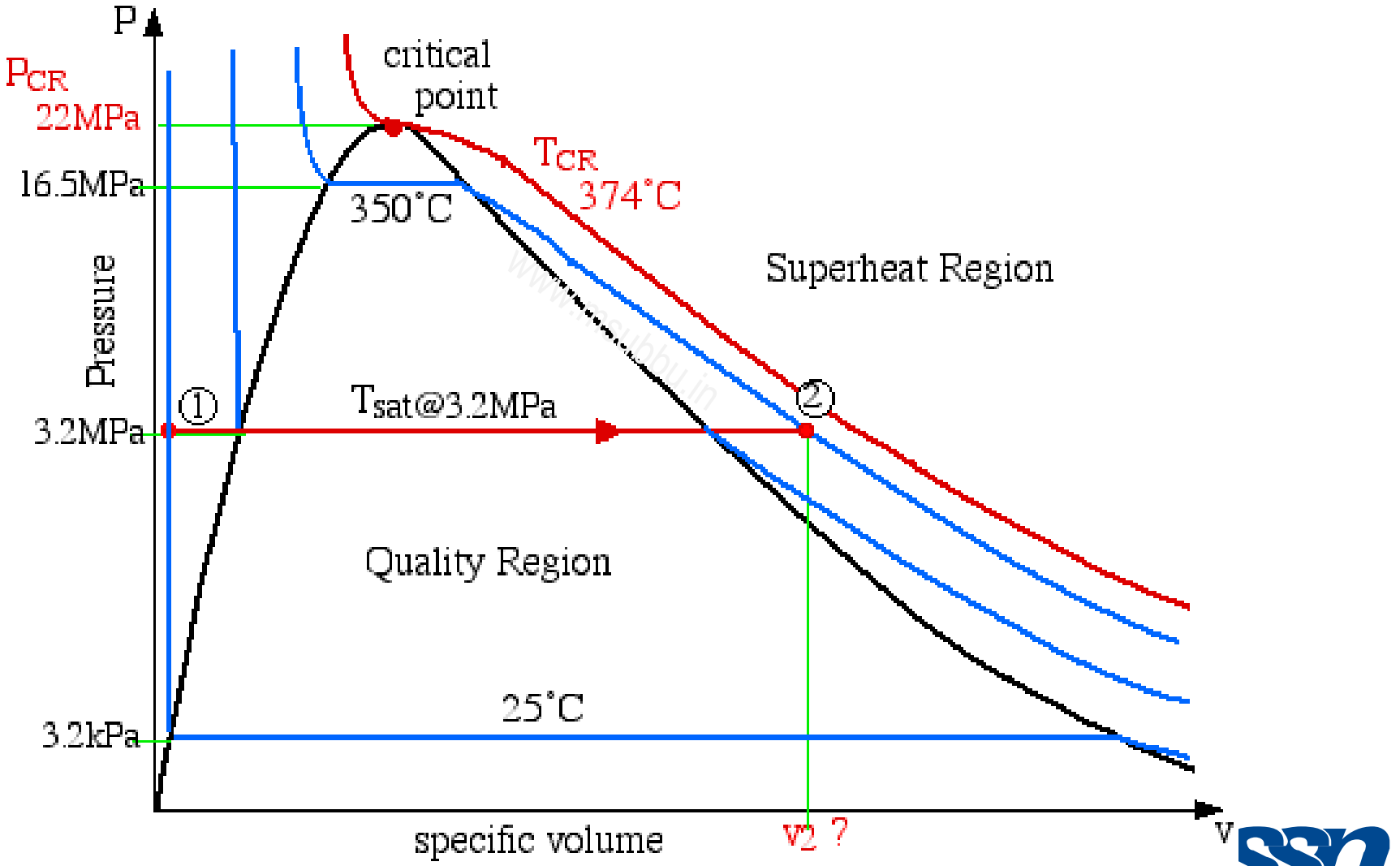

T-v diagram for water
Temperature (deg C)
Specific Volume (m3/kg)
600
500
400
300
200
100
20
0
0.001
0.01
0.1
1
10
20°C
100°C
100°C
100°C
300°C
100kPa
1
2
3
4
5
plot by izzi
www.msubau.in

Two kilograms of water at 25°C are placed in a piston cylinder device under 3.2 MPa pressure as shown in the diagram (State (1)). Heat is added to the water at constant pressure until the temperature of the fluid reaches 350°C (State (2)). Determine the final volume of the fluid at state (2).



http://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter2a.html

In this example since the pressure is known (3.2 MPa) and remains constant throughout the process, we find it convenient to draw a *P-v* diagram indicating the process (1) - (2) as follows.



	P=3.0 MPa (233.9°C)				P=3.5 MPa (242.6°C)			
Temp	volume	energy	enthalpy	entropy	volume	energy	enthalpy	entropy
°C	v(m^3/kg)	u(kJ/kg)	h(kJ/kg)	s(kJ/kg.K)	v(m^3/kg)	u(kJ/kg)	h(kJ/kg)	s(kJ/kg.K)
Sat.	0.0667	2603.2	2803.2	6.186	0.0571	2602.9	2802.6	6.124
250	0.0706	2644.7	2856.5	6.289	0.0588	2624.0	2829.7	6.176
300	0.0812	2750.8	2994.3	6.541	0.0685	2738.8	2978.4	6.448
350	0.0906	2844.4	3116.1	6.745	0.0768	2836.0	3104.8	6.660
400	0.0994	2933.5	3231.7	6.923	0.0846	2927.2	3223.2	6.843
450	0.1079	3021.2	3344.8	7.086	0.0920	3016.1	3338.0	7.007
500	0.1162	3108.6	3457.2	7.236	0.0992	3104.5	3451.6	7.159
600	0.1325	3285.5	3682.8	7.510	0.1133	3282.5	3678.9	7.436
700	0.1484	3467.0	3912.2	7.759	0.1270	3464.7	3909.3	7.685
800	0.1642	3654.3	4146.9	7.989	0.1406	3652.5	4144.6	7.916
900	0.1799	3847.9	4387.5	8.203	0.1541	3846.4	4385.7	8.130
1000	0.1955	4047.7	4634.1	8.405	0.1675	4046.4	4632.7	8.332

http://www.ohio.edu/mechanical/thermo/property_tables/H2O/H2O_Super3.html (18-Aug-2012)

We find that we need to interpolate between pressure P = 3.0 MPa and P = 3.5 MPa in order to determine the specific volume at the required pressure of 3.2 MPa as follows:

Superheat Vapor Tables

P	3.0	3.2	3.5	MPa
T_{sat}	233.9°C	237.4°C	242.6°C	
v @ 350°C	0.0906	0.085	0.0768	m^3/kg

$$\frac{(T_{sat} - 233.9)^\circ C}{(242.6 - 233.9)^\circ C} = \frac{(3.2 - 3.0)\ MPa}{(3.5 - 3.0)\ MPa} = 0.4$$

$$\Rightarrow T_{sat} = 237.4^\circ C$$

$$\frac{(0.0906 - v_2)\ [m^3/kg]}{(0.0906 - 0.0768)\ [m^3/kg]} = \frac{(3.2 - 3.0)\ MPa}{(3.5 - 3.0)\ MPa} = 0.4$$

$$\Rightarrow v_2 = 0.085\ [m^3/kg]$$

$$V_2 = m.v_2 \Rightarrow 0.170\ [m^3]$$

From the corresponding state principle by considering Z as a function of (T_r, P_r) estimate the volume of 1 kmol of oxygen at 200 K and 6 x 10^6 N/m^2. (P_c = 5.05 x 10^6 N/m^2; T_c = 155 K). Z values for various T_r, P_r are as given below:

	Z			
T_r P_r →	**0.8**	**1.0**	**1.2**	**1.5**
1.1 ↓	0.7649	0.6880	0.5984	0.4580
1.2	0.8330	0.7858	0.7363	0.6605
1.3	0.8764	0.8438	0.8111	0.7624
1.4	0.9062	0.8827	0.8595	0.8256
1.5	0.9278	0.9103	0.8933	0.8689

First by considering the interpolation at fixed values of Pr, get Z; then at fixed Tr value get the Z.
That way, you will get **Z** as **0.807**