CH2303 Chemical Engineering Thermodynamics I

Unit – IV

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Thermodynamic Property Relations

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Contents

- Measurable quantities, basic energy relations, Maxwell relations,
- Thermodynamic formulations to calculate enthalpy, internal energy and entropy as function of pressure and temperature,
- Other formulations involving Cp and Cv, complex thermodynamic formulations,

Mathematical Relations

$$F = F(x, y)$$

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

$$dF = M dx + N dy$$

$$\frac{\partial^2 F}{\partial y \partial x} = \frac{\partial^2 F}{\partial x \partial y}$$

exactness criteria:

$$\left(\frac{\partial M}{\partial y}\right)_x - \left(\frac{\partial N}{\partial x}\right)_y$$

Cyclic Relation Rule

For the function in the variables x, y & z

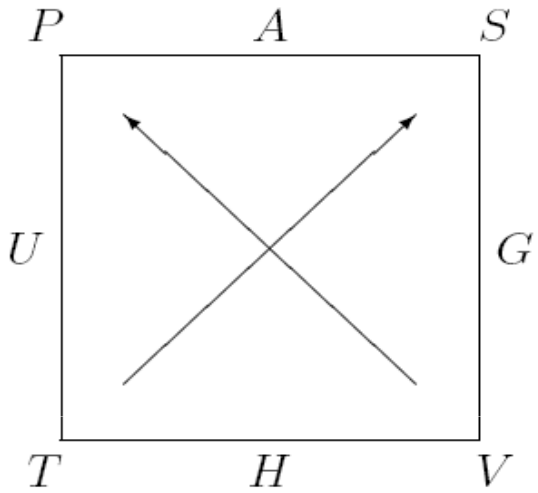
$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Other Relations of Importance

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

fundamental property relations:

$$
\begin{aligned}
dU &= TdS - PdV \\
dH &= VdP + TdS \\
dG &= -SdT + VdP \\
dA &= -PdV - SdT
\end{aligned}
$$



PASGVHTU

Maxwell Relations

$$
\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\
\left(\frac{\partial V}{\partial S}\right)_P &= \left(\frac{\partial T}{\partial P}\right)_S \\
\left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P \\
\left(\frac{\partial P}{\partial T}\right)_V &= \left(\frac{\partial S}{\partial V}\right)_T
\end{aligned}
$$

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_V = C_V}$$

$$\boxed{\left(\frac{\partial H}{\partial T}\right)_P = C_P}$$

$$V = V(T, P)$$

$$\frac{dV}{V} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P dT + \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\frac{dV}{V} = \beta dT - \kappa dP$$

$$\beta = \text{Volume expansivity} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\kappa = \text{Isothermal compressibility} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Relations for dU

$$U = U(T, V)$$

$$dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

Relations for dH

$$H = H(T, P)$$

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

Relations for dS

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$
$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$S = S(T, V)$$

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$S = S(T, P)$$

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

Relations for Specific heats

$$C_P = T\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_V = -T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S$$

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2$$

$$\frac{C_P}{C_V} = \frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T}$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Two-phase Systems

$$d(nG) = (nV)dP - (nS)dT$$

During phase change T and P remains constant. Therefore, $d(nG) = 0$. Since $dn \neq 0$, $dG = 0$.

For two phases α and β of a pure species coexisting at equilibrium:

$$G^{\alpha} = G^{\beta}$$

$$dG^{\alpha} = dG^{\beta}$$

$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

Clapeyon equation

$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$

Clausius-Clapeyron equation

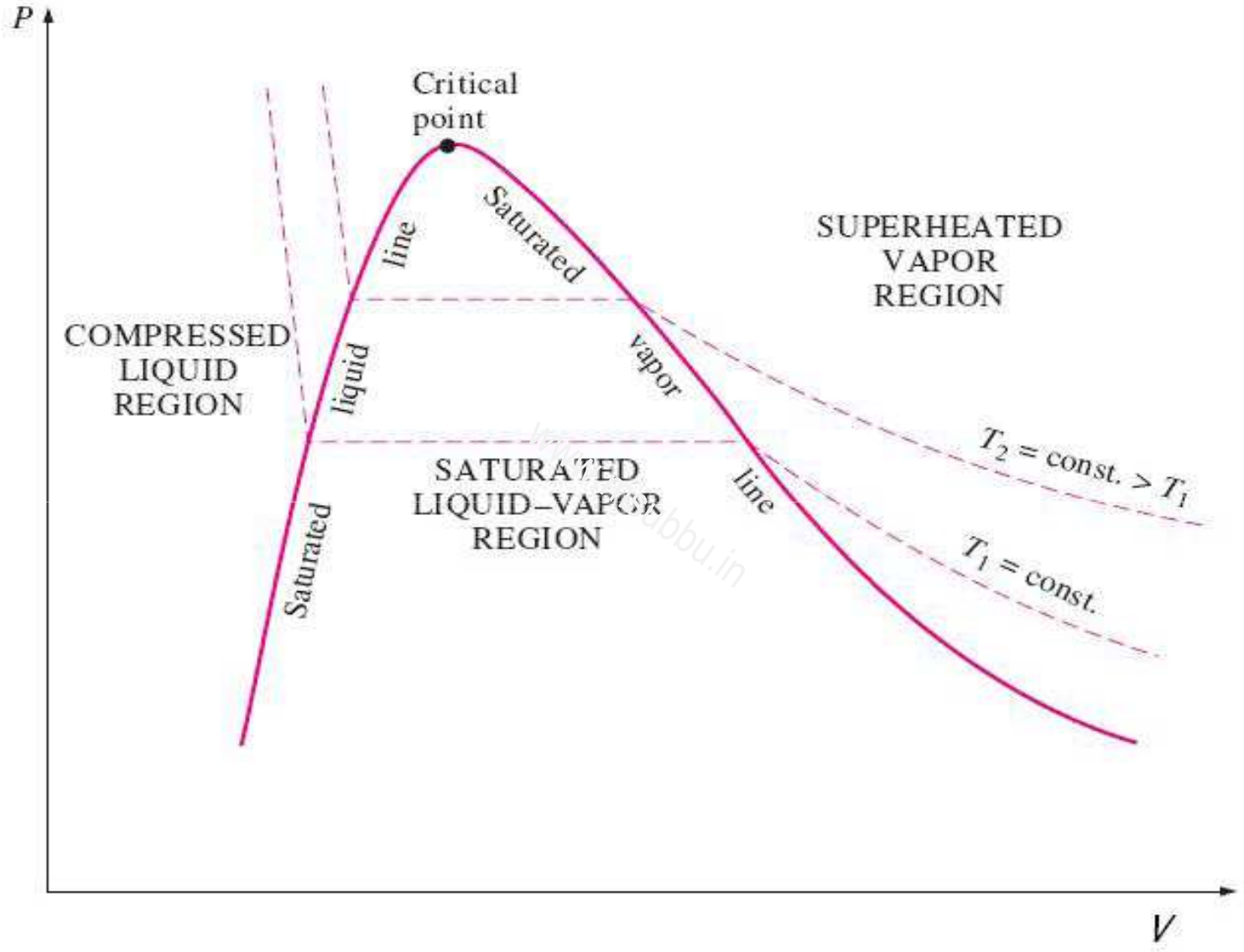
$$\ln \frac{P_2^{\text{sat}}}{P_1^{\text{sat}}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

From Clausius-Clapeyron equation

$$\ln P^{\text{sat}} = A - \frac{B}{T}$$

A satisfactory relation given by *Antoine* is of the form

$$\ln P^{\text{sat}} = A - \frac{B}{T + C}$$


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

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

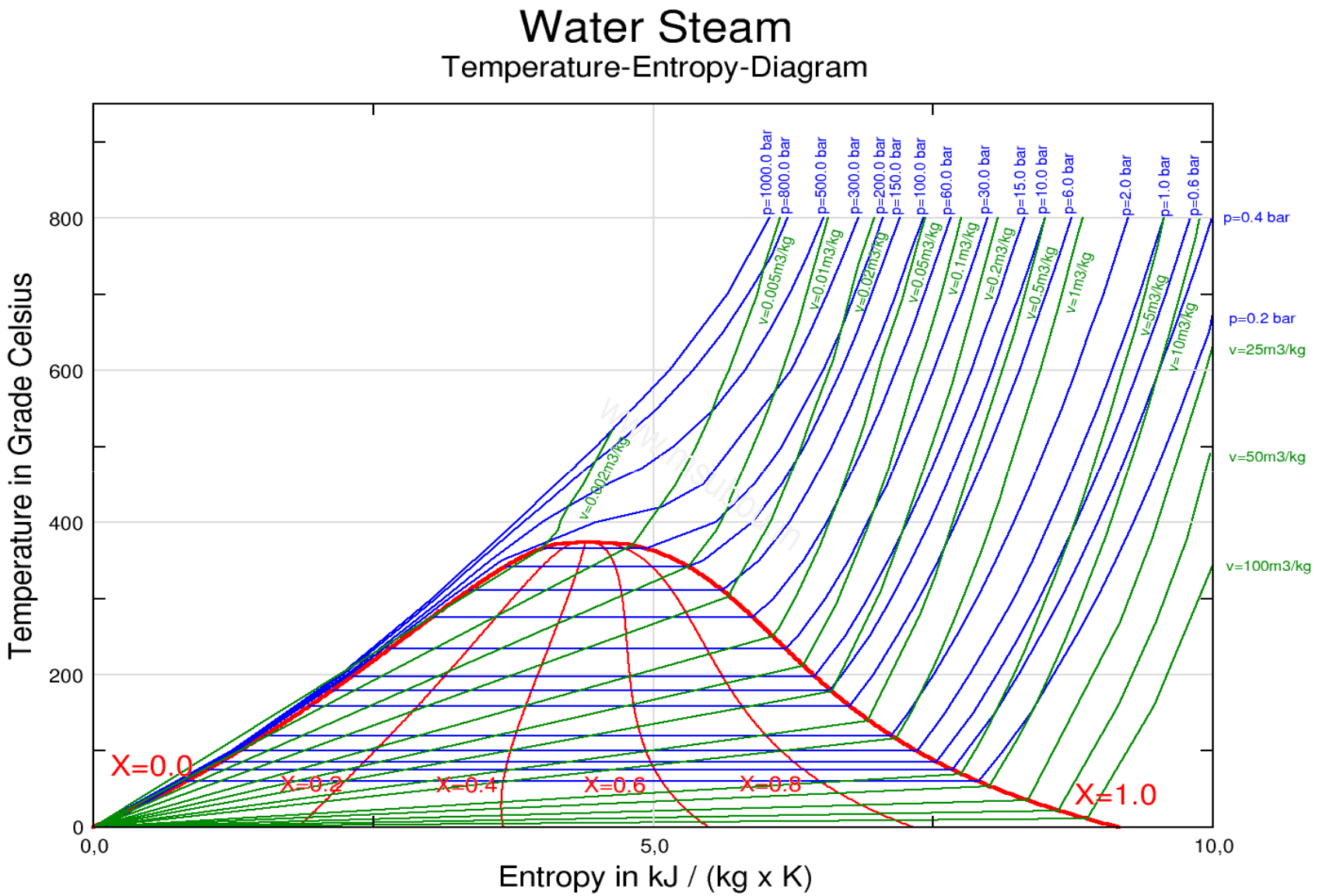
Single-phase tables

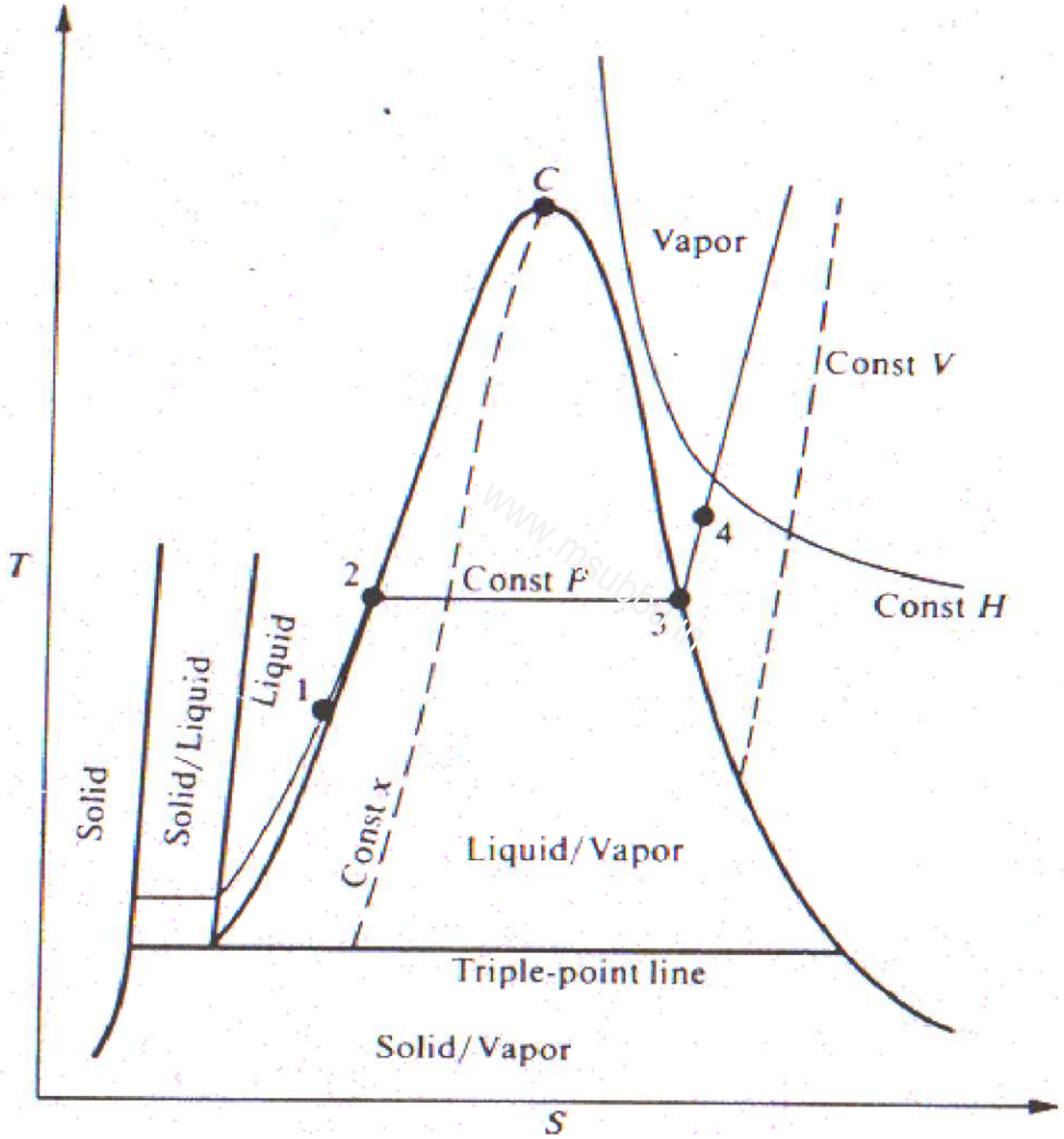
TABLE A.1.3SI *Superheated Vapor Water (SI Units)*

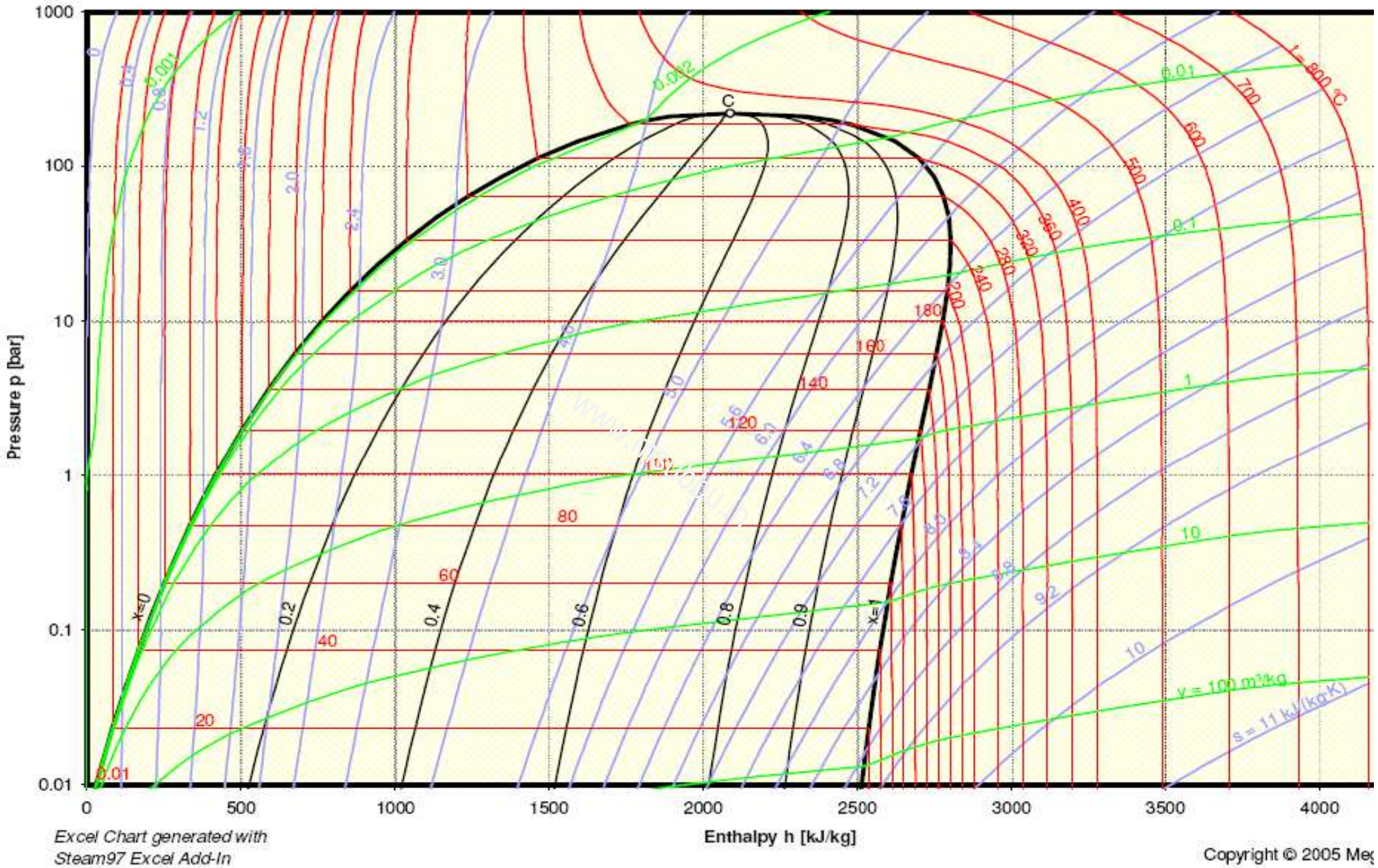
	P = 10 kPa (45.81)				P = 50 kPa (81.33)			
T	v	u	h	s	v	u	h	s
Sat.	14.674	2437.9	2584.6	8.1501	3.240	2483.8	2645.9	7.593
50	14.869	2443.9	2592.6	8.1749	—	—	—	—
100	17.196	2515.5	2687.5	8.4479	3.418	2511.6	2682.5	7.694
150	19.513	2587.9	2783.0	8.6881	3.889	2585.6	2780.1	7.940
200	21.825	2661.3	2879.5	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	3.359
0	.0009977	0.03	5.02	0.0001	.0009952	0.10	10.05	0.000
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


Water Steam
Temperature-Entropy-Diagram
Temperature in Grade Celsius
Entropy in kJ / (kg x K)
0
200
400
600
800
0,0
5,0
10,0
p=1000.0 bar
p=800.0 bar
p=500.0 bar
p=300.0 bar
p=200.0 bar
p=150.0 bar
p=100.0 bar
p=60.0 bar
p=30.0 bar
p=15.0 bar
p=10.0 bar
p=6.0 bar
p=2.0 bar
p=1.0 bar
p=0.6 bar
p=0.4 bar
p=0.2 bar
v=0.005m3/kg
v=0.01m3/kg
v=0.02m3/kg
v=0.05m3/kg
v=0.1m3/kg
v=0.2m3/kg
v=0.5m3/kg
v=1m3/kg
v=5m3/kg
v=10m3/kg
v=25m3/kg
v=50m3/kg
v=100m3/kg
v=0.002m3/kg
X=0.0
X=0.2
X=0.4
X=0.6
X=0.8
X=1.0


C
Vapor
Const V
T
2
Const P
4
Const H
3
1
Liquid
Solid/Liquid
Solid
Const x
Liquid/Vapor
Triple-point line
Solid/Vapor
S


Pressure p [bar]
Enthalpy h [kJ/kg]
1000
100
10
1
0.1
0.01
0
500
1000
1500
2000
2500
3000
3500
4000
C
x=0
x=1
0.2
0.4
0.6
0.8
0.9
0.01
0.001
0.0012
0.1
1
10
100
v = 100 m³/kg
s = 11 kJ/(kg·K)
t = 800 °C
700
600
500
400
360
320
280
240
200
180
160
140
120
100
80
60
40
20
Excel Chart generated with
Steam97 Excel Add-In
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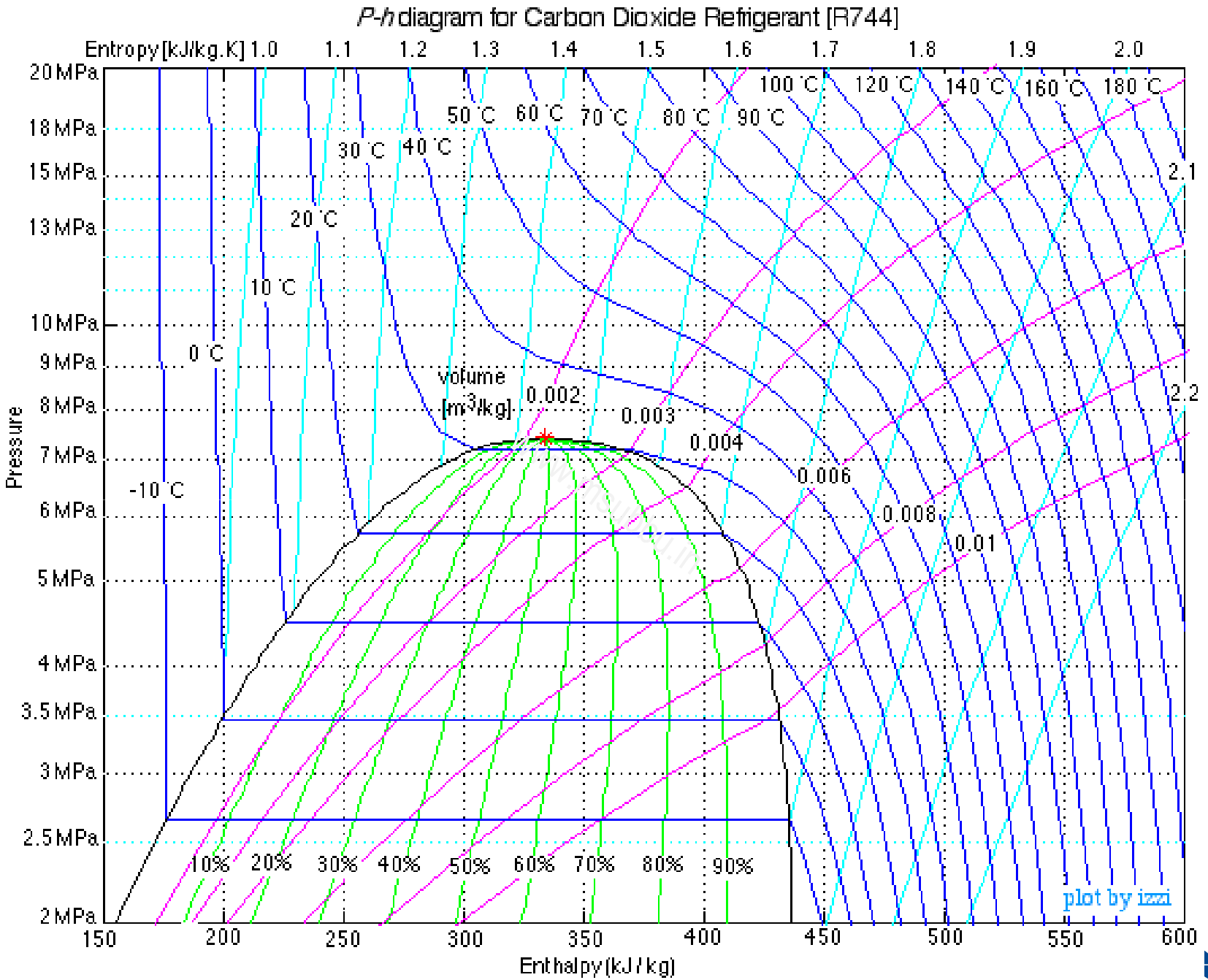
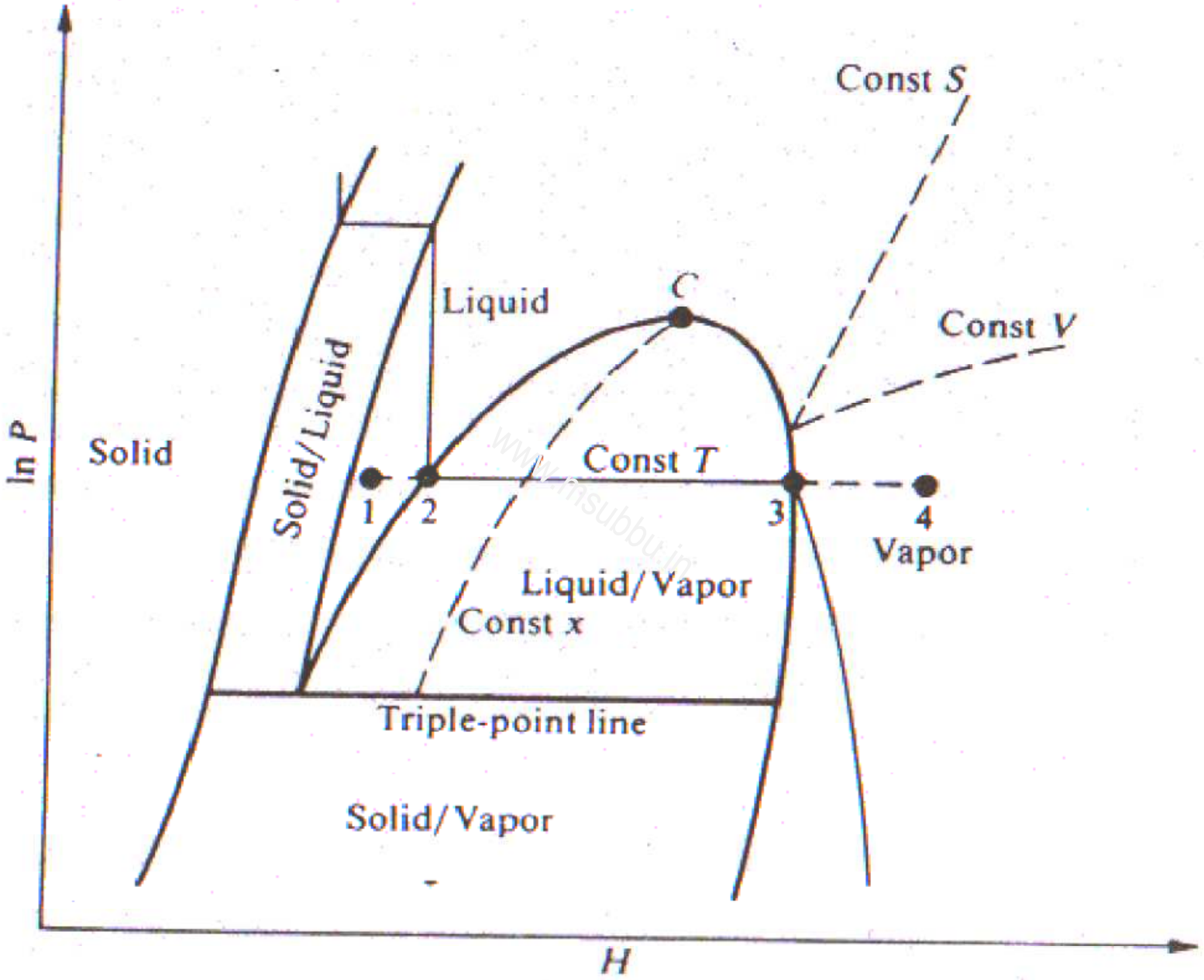
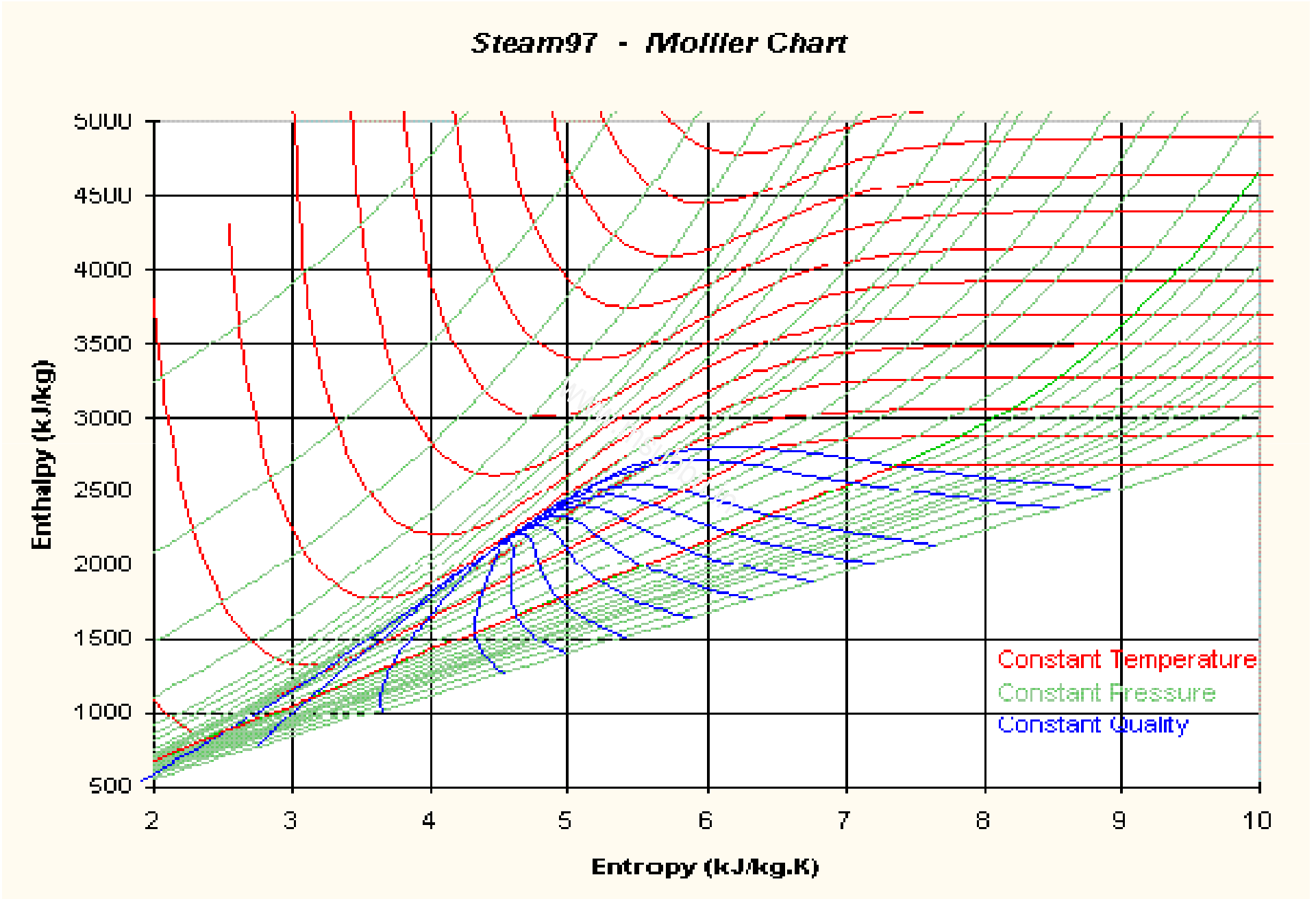
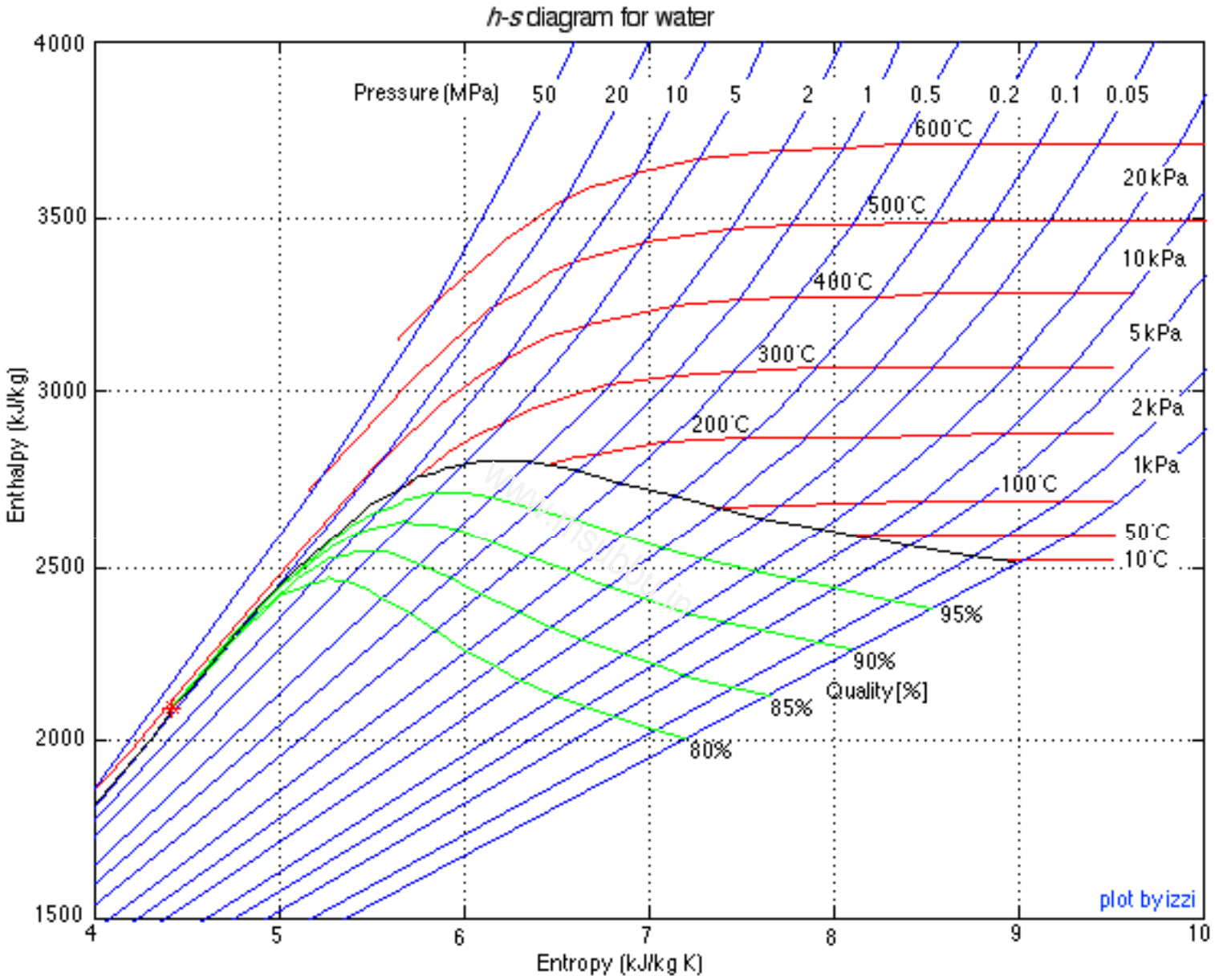
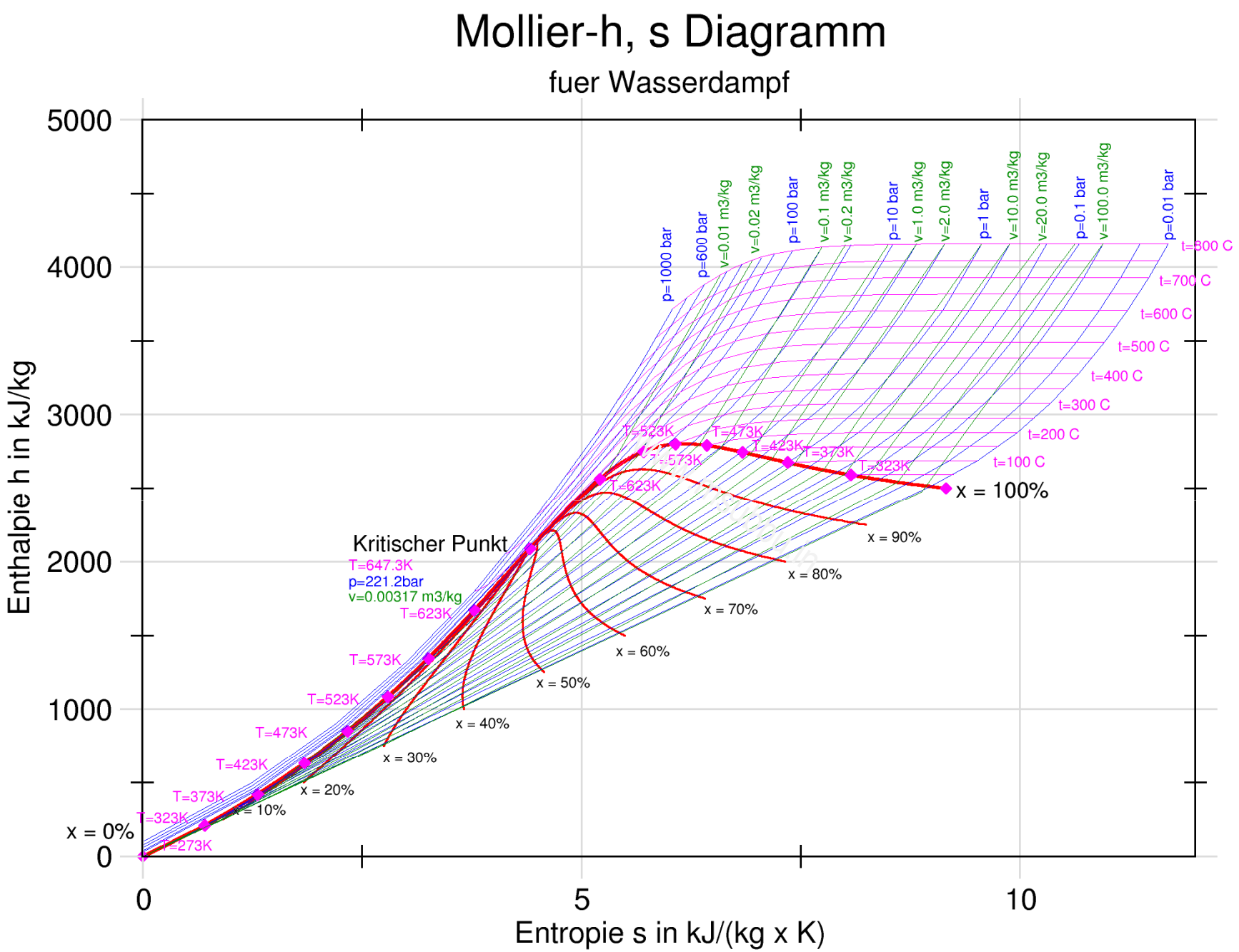

P-h diagram for Carbon Dioxide Refrigerant [R744]
Entropy [kJ/kg.K]
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
20 MPa
18 MPa
15 MPa
13 MPa
10 MPa
9 MPa
8 MPa
7 MPa
6 MPa
5 MPa
4 MPa
3.5 MPa
3 MPa
2.5 MPa
2 MPa
Pressure
100 °C
120 °C
140 °C
160 °C
180 °C
50 °C
60 °C
70 °C
80 °C
90 °C
30 °C
40 °C
20 °C
10 °C
0 °C
-10 °C
2.1
2.2
volume
[m3/kg]
0.002
0.003
0.004
0.006
0.008
0.01
10%
20%
30%
40%
50%
60%
70%
80%
90%
plot by izzi
150
200
250
300
350
400
450
500
550
600
Enthalpy (kJ/kg)


Const S
Liquid
C
Const V
ln P
Solid
Solid/Liquid
Const T
1
2
3
4
Vapor
Liquid/Vapor
Const x
Triple-point line
Solid/Vapor
H


Steam97 - Mollier Chart
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
Enthalpy (kJ/kg)
2
3
4
5
6
7
8
9
10
Entropy (kJ/kg.K)
Constant Temperature
Constant Pressure
Constant Quality


h-s diagram for water
Pressure (MPa)
50
20
10
5
2
1
0.5
0.2
0.1
0.05
600°C
500°C
400°C
300°C
200°C
100°C
50°C
10°C
20 kPa
10 kPa
5 kPa
2 kPa
1kPa
95%
90%
85%
80%
Quality [%]
Enthalpy (kJ/kg)
Entropy (kJ/kg K)
4000
3500
3000
2500
2000
1500
4
5
6
7
8
9
10
plot by izzi


Mollier-h, s Diagramm
fuer Wasserdampf
Enthalpie h in kJ/kg
Entropie s in kJ/(kg x K)
5000
4000
3000
2000
1000
0
0
5
10
p=1000 bar
p=600 bar
v=0.01 m3/kg
v=0.02 m3/kg
p=100 bar
v=0.1 m3/kg
v=0.2 m3/kg
p=10 bar
v=1.0 m3/kg
v=2.0 m3/kg
p=1 bar
v=10.0 m3/kg
v=20.0 m3/kg
p=0.1 bar
v=100.0 m3/kg
p=0.01 bar
t=800 C
t=700 C
t=600 C
t=500 C
t=400 C
t=300 C
t=200 C
t=100 C
T=523K
T=473K
T=423K
T=373K
T=323K
T=573K
T=623K
x = 100%
x = 90%
x = 80%
x = 70%
x = 60%
x = 50%
x = 40%
x = 30%
x = 20%
x = 10%
x = 0%
T=273K
Kritischer Punkt
T=647.3K
p=221.2bar
v=0.00317 m3/kg

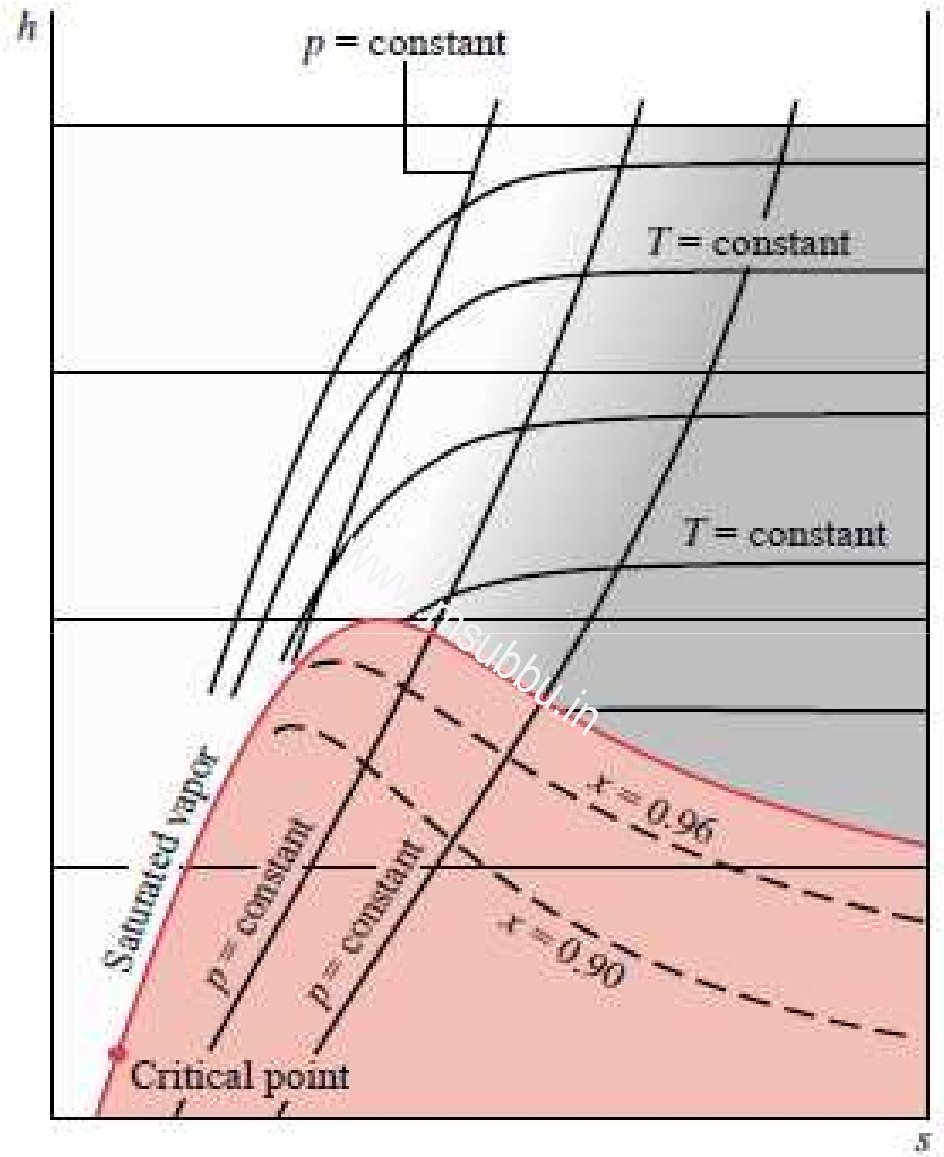


Figure 7.4 Enthalpy–entropy diagram.

Developing Thermodynamic Diagrams

TS Diagram

Experimental Data:

(a) Vapor pressure data.

(b) Pressure, specific volume, temperature ($\boldsymbol{PVT}$) data in the vapor region.

(c) Density of saturated liquid and the critical pressure and temperature.

(d) Zero pressure specific heat data for the vapor.

1. Relation for $\ln \boldsymbol{P}^{\text{sat}}$ vs. $\boldsymbol{T}$ such as

$$\ln \boldsymbol{P}^{\text{sat}} = \boldsymbol{A} - \frac{\boldsymbol{B}}{\boldsymbol{T} + \boldsymbol{C}}$$

2. Equation of state for the vapor that accurately represents the $\boldsymbol{PVT}$ data.

3. **State: 1**
   Fix values for $\boldsymbol{H}$ and $\boldsymbol{S}$ of saturated-liquid at a reference state.

4. **State: 2**
   Enthalpy and entropy changes during vaporization are calculated from Clapeyron equation using the $\ln \boldsymbol{P}^{\text{sat}}$ vs. $\boldsymbol{T}$ data as:

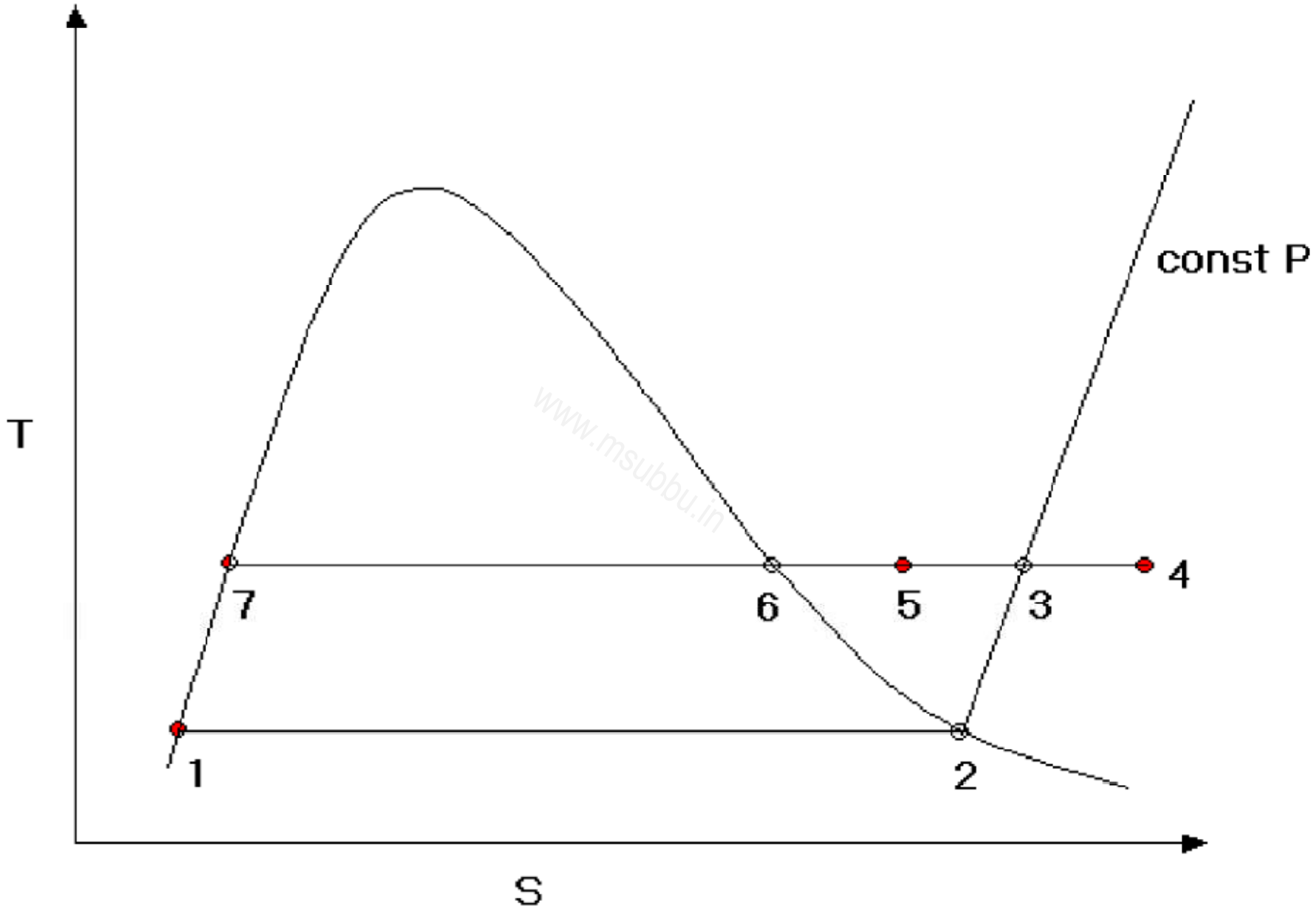
$$\frac{d\boldsymbol{P}^{\text{sat}}}{d\boldsymbol{T}} = \frac{\boldsymbol{\Delta H_{lv}}}{\boldsymbol{T}(\boldsymbol{V_v} - \boldsymbol{V_l})}$$

   and

$$\boldsymbol{\Delta S_{lv}} = \frac{\boldsymbol{\Delta H_{lv}}}{\boldsymbol{T}}$$

   Here $\boldsymbol{V_l}$ shall be measured, and $\boldsymbol{V_v}$ is calculated from the relation obtained in step-2.

   From these values of $\boldsymbol{\Delta H_{vl}}$ and $\boldsymbol{\Delta S_{vl}}$ obtaine the values of $\boldsymbol{H}$ and $\boldsymbol{S}$ at state: 2



5. **State: 3** Follow the constant pressure line.

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

Here for the specific heat of vapor corresponding to the pressure at state: 2 is obtained from the relation:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)$$

and from the zero pressure specific heat data.

With the value of C_P for this state as calculated above, S and H values at state: 3 are calculated.

6. **State: 4, 5 & 6** The above calculation can be done along constant temperature lineand the values at states 4, 5 and 6 can be obtained.

7. **State: 7** The calculations made for state: 2 can de done for the temperature at state: 6.