Properties of Pure Substances

Chapter 3

Objectives

- Introduce the concept of a pure substance
- Discuss the physics of phase-change processes
- Illustrate the P-v, T-v and P-T diagram
- Demonstrate the procedures for determining thermodynamic properties from tables

Pure Substance

- **Chemistry: as an element or a compound and it can't be separated**

- **Thermodynamics: as something that has a fixed chemical composition**

Examples

- Water, N_2, He, CO_2, etc.
- Ice in equilibrium with water

Phases of Pure Substances

Solid - copper

Liquid - mercury

Gas – nitrogen

Solid

- Three dimensional pattern
- Large attractive forces between atoms or molecules – small distance
- The atoms or molecules are in constant motion – they vibrate in place
- The higher the temperature – the more vibration

Liquid

- When a solid reaches a high enough temperature the vibrations are strong enough to break the strong forces between molecules – melting process

  - not fixed position; chunk of molecules floating
  - Forces are weaker than solid

Gas

- Molecules are far apart
- High kinetic energy
- In order to liquefy, lots of that kinetic energy must be released

Phase-change Processes of Pure Substances

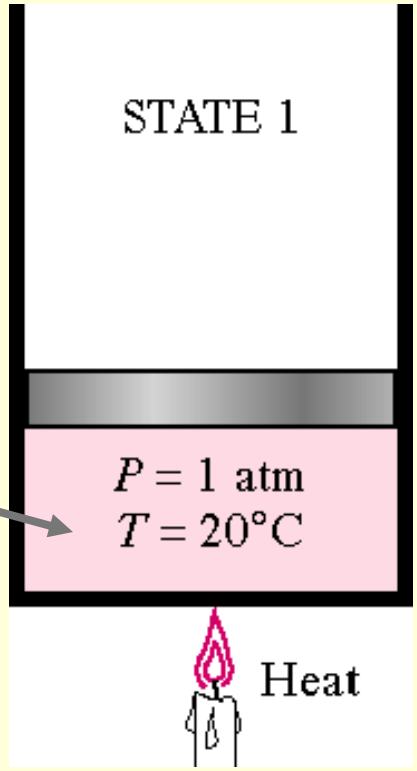
compressible liquid

saturated liquid

saturated vapor

superheated vapor

Consider what happens when we heat water at constant pressure



Liquid Water

Piston cylinder device – maintains constant pressure

Phase-change Processes of Pure Substances

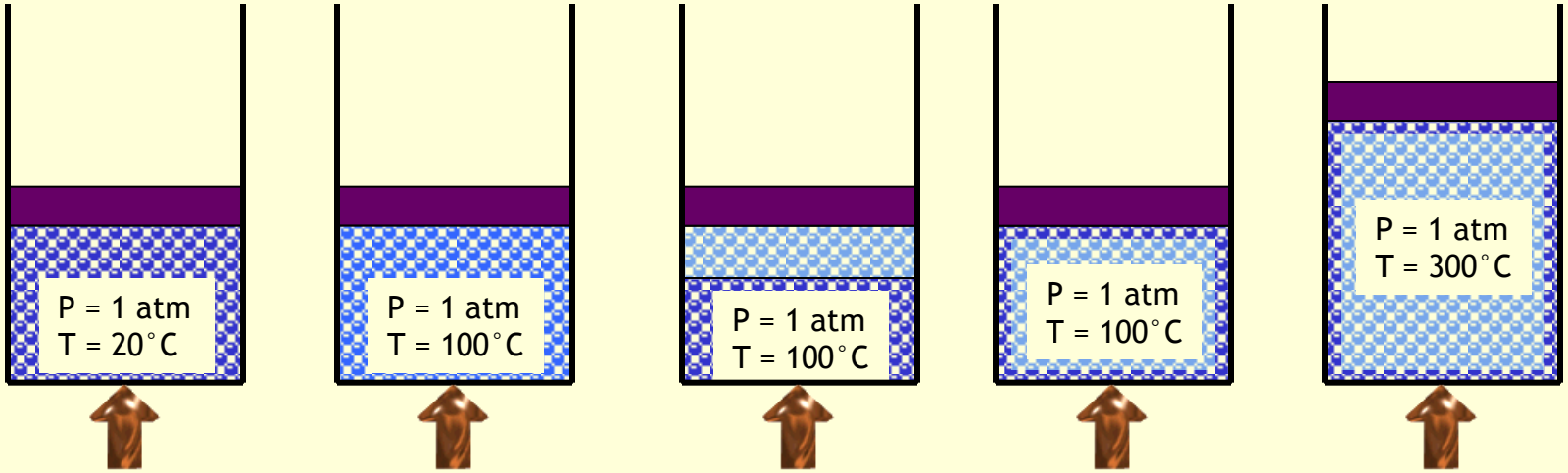


Fig. 3.1 Fig. 3.2 Fig. 3.3 Fig. 3.4 Fig. 3.5

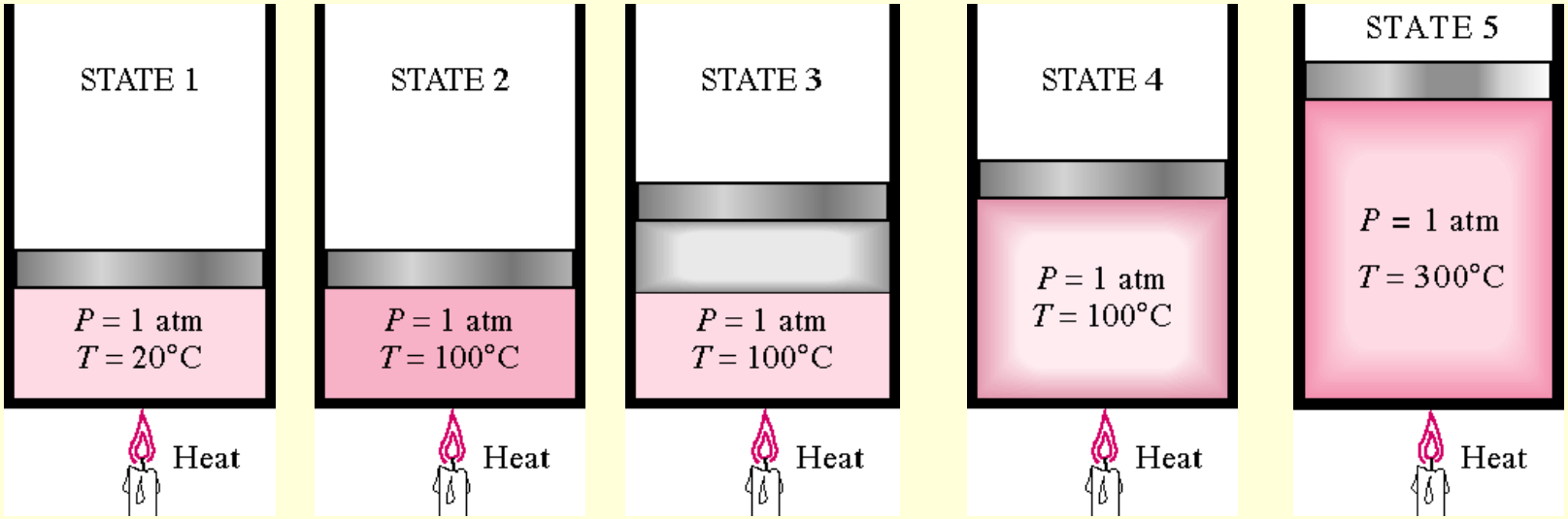
Fig 3.1 At 1 atm and 20ºC water exists in the liquid phase (compressible liquid) Table A-7

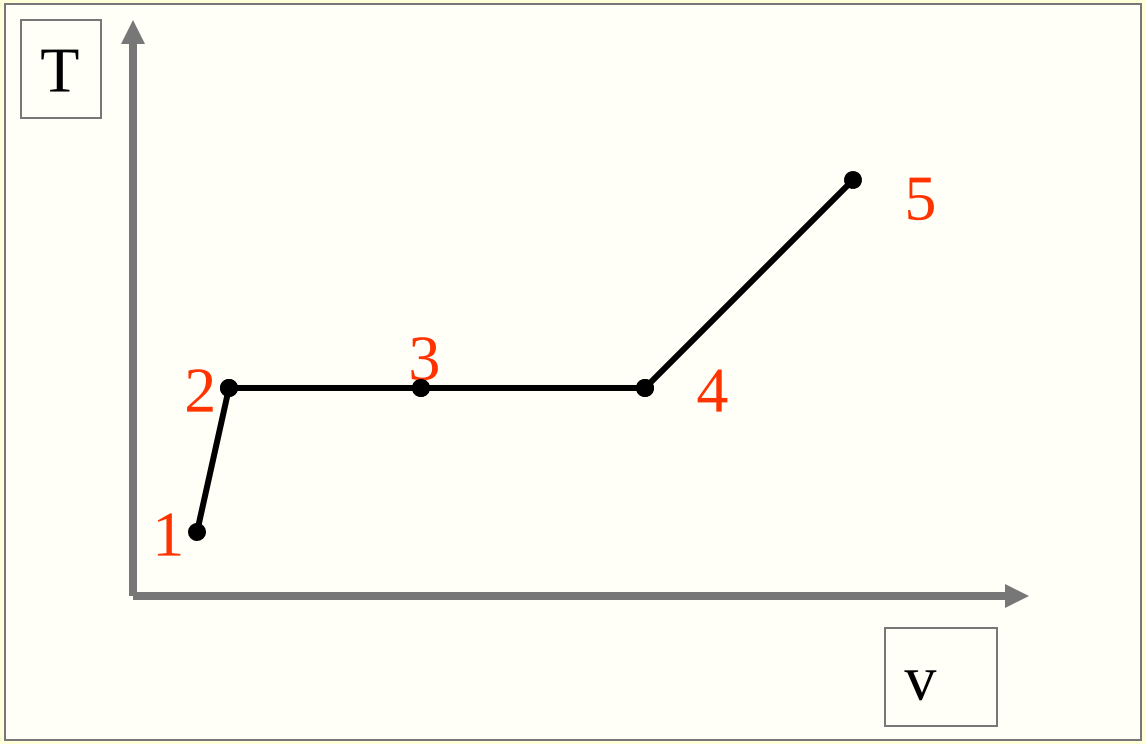
Fig. 3.2 At 1 atm pressure and 100ºC, water exists as a liquid which is ready to vaporize (saturated liquid) Table A-4

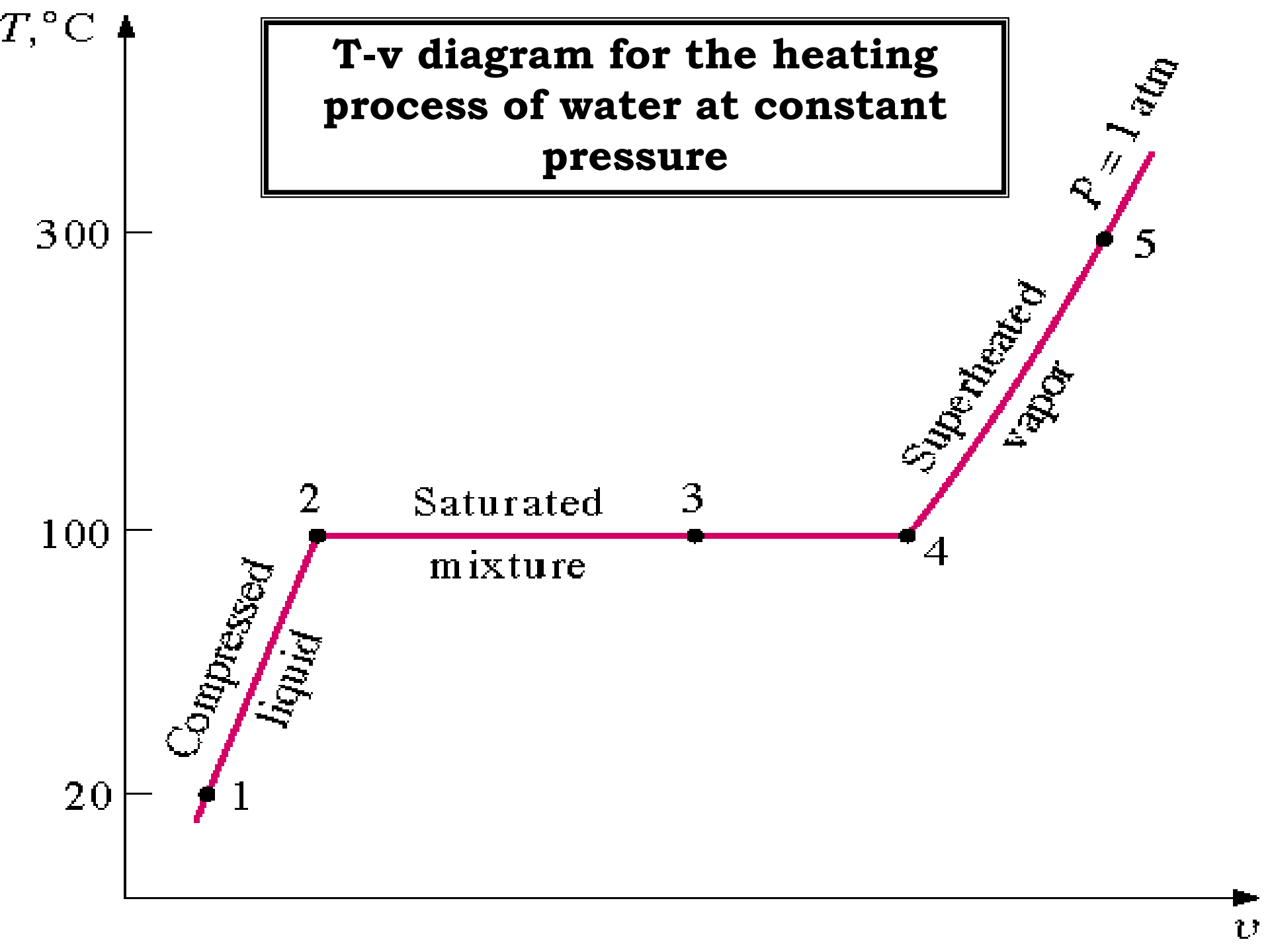
Fig. 3.3 As more heat is transferred, part of saturated liquid vaporizes (saturated liquid-vapor mixture) Table A-4

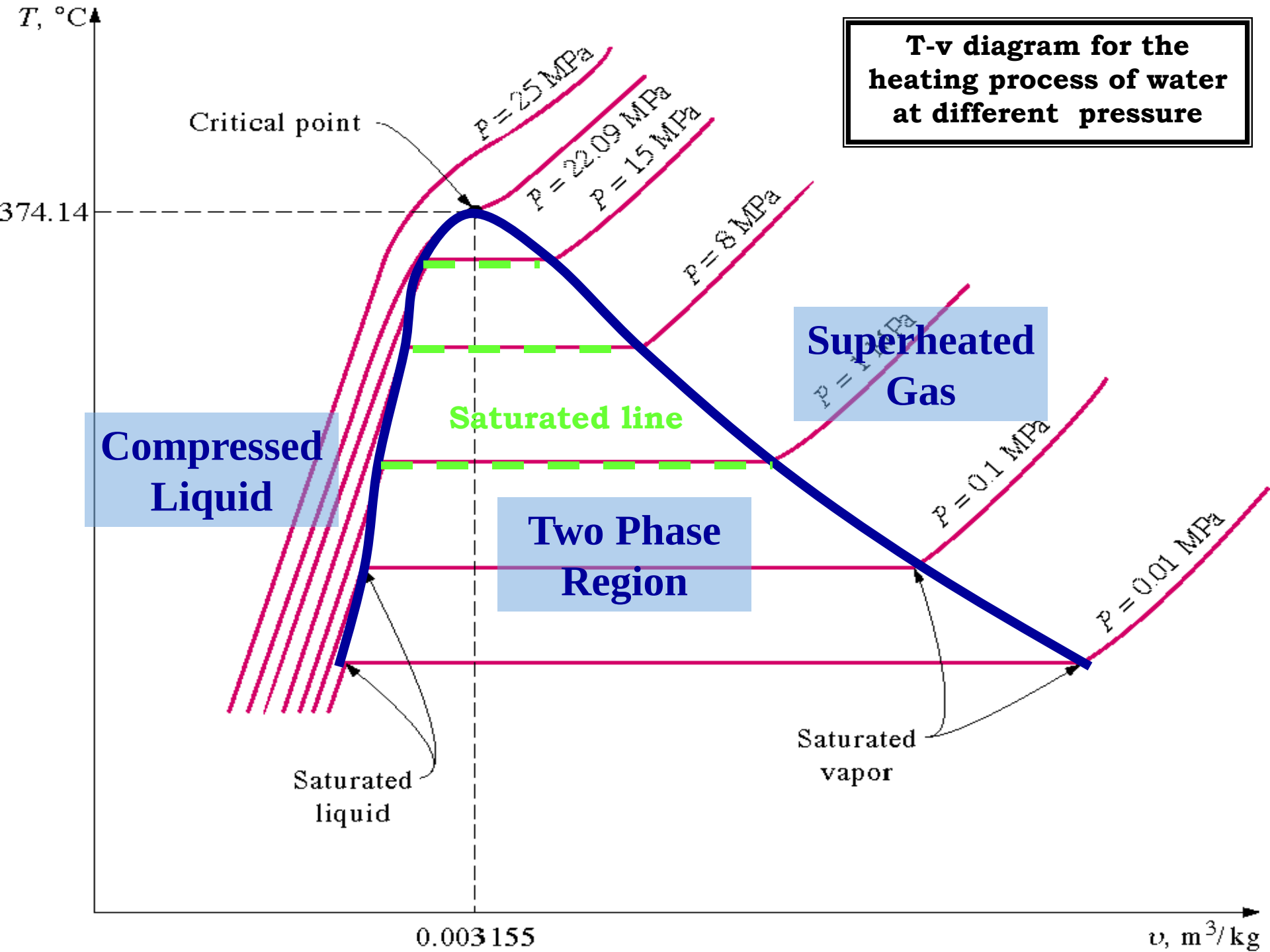
Fig. 3.4 At 1-atm pressure, the temperature remains constant at 100ºC until the last drop of liquid is vaporized (saturated vapor) Table A-4

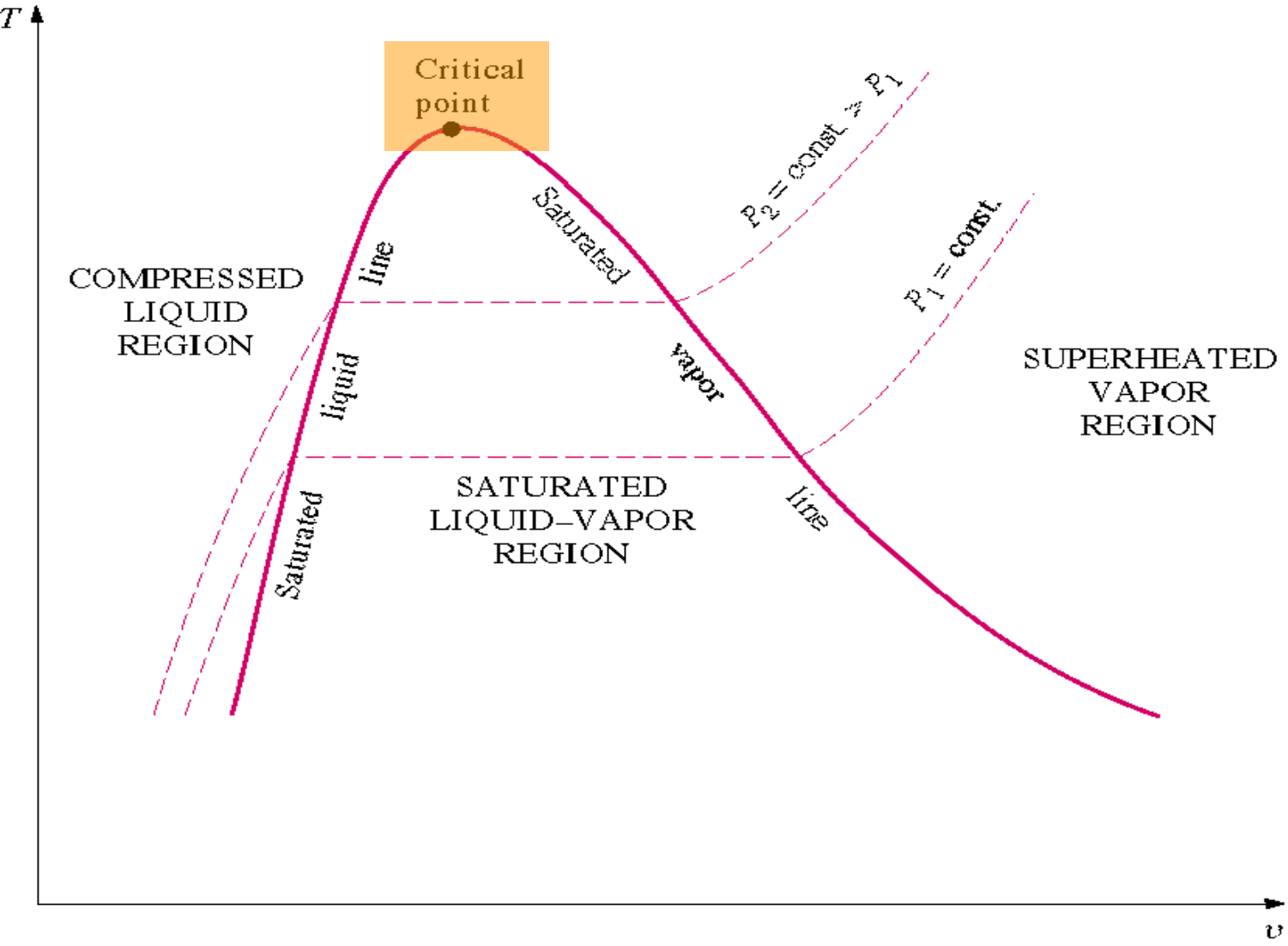
Fig. 3.5 As more heat is transferred, the temperature of the vapor starts to rise (superheated vapor) Table A-6


STATE 1
P = 1 atm
T = 20°C
Heat
STATE 2
P = 1 atm
T = 100°C
Heat
STATE 3
P = 1 atm
T = 100°C
Heat
STATE 4
P = 1 atm
T = 100°C
Heat
STATE 5
P = 1 atm
T = 300°C
Heat


T
v
1
2
3
4
5


T-v diagram for the heating process of water at constant pressure
T, °C
300
100
20
1
2
3
4
5
Compressed liquid
Saturated mixture
Superheated vapor
P = 1 atm
v


T-v diagram for the heating process of water at different pressure
T, °C
374.14
Critical point
p = 25 MPa
p = 22.09 MPa
p = 15 MPa
p = 8 MPa
p = 1 MPa
p = 0.1 MPa
p = 0.01 MPa
Superheated Gas
Saturated line
Compressed Liquid
Two Phase Region
Saturated liquid
Saturated vapor
0.003155
v, m³/kg



As increases pressure, the shorter the saturation line ; pressure reaches 22.09 MPa (water) and at this point, it is called critical point

critical point ; the point at which the saturated liquid and the saturated vapor states are identical

Critical Point

- Above the critical point there is no sharp difference between liquid and gas!!

- Critical point of several substances can be found in Appendix Table A.1

  – E.g for NH_3

$T_c = 405.5$ K

$P_c = 11.28$ MPa

$v_c = 0.0724$ $m^3/kmol$

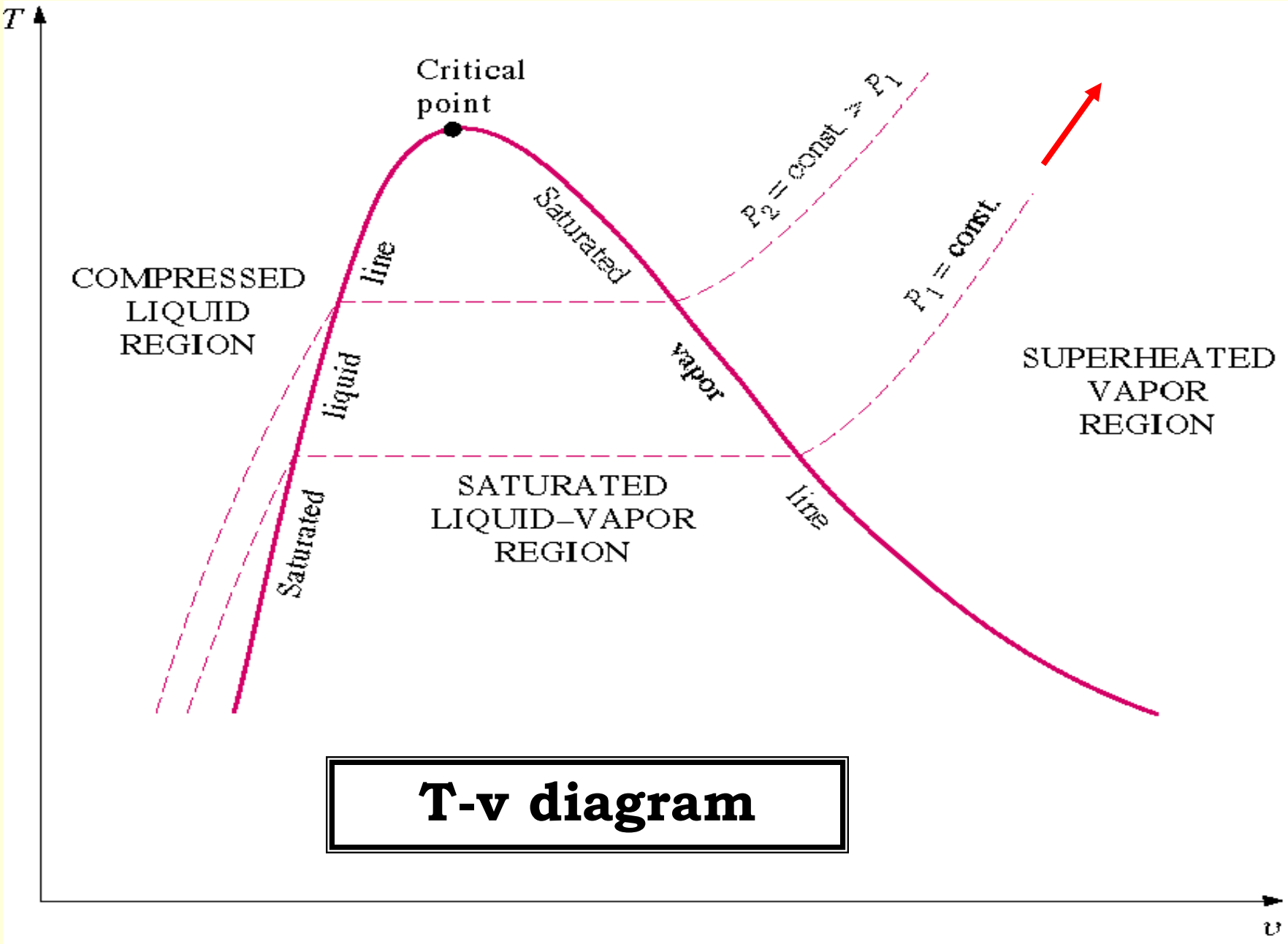
Critical Point

- Critical point of several substances can be found in Appendix Table A.1
  - E.g for O_2

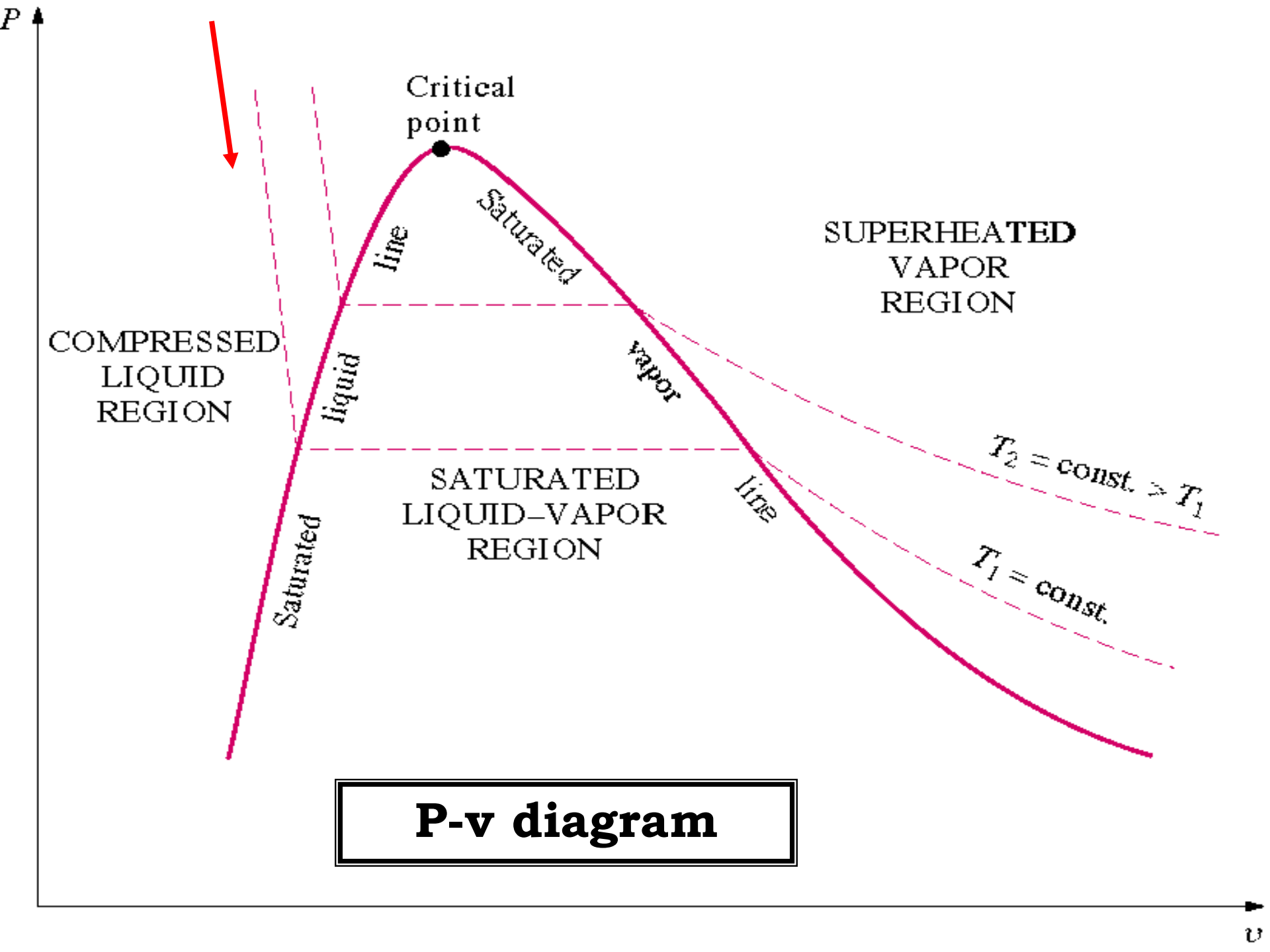
T_c = ? K

P_c = ? MPa

ν_c = ? m^3/kmol

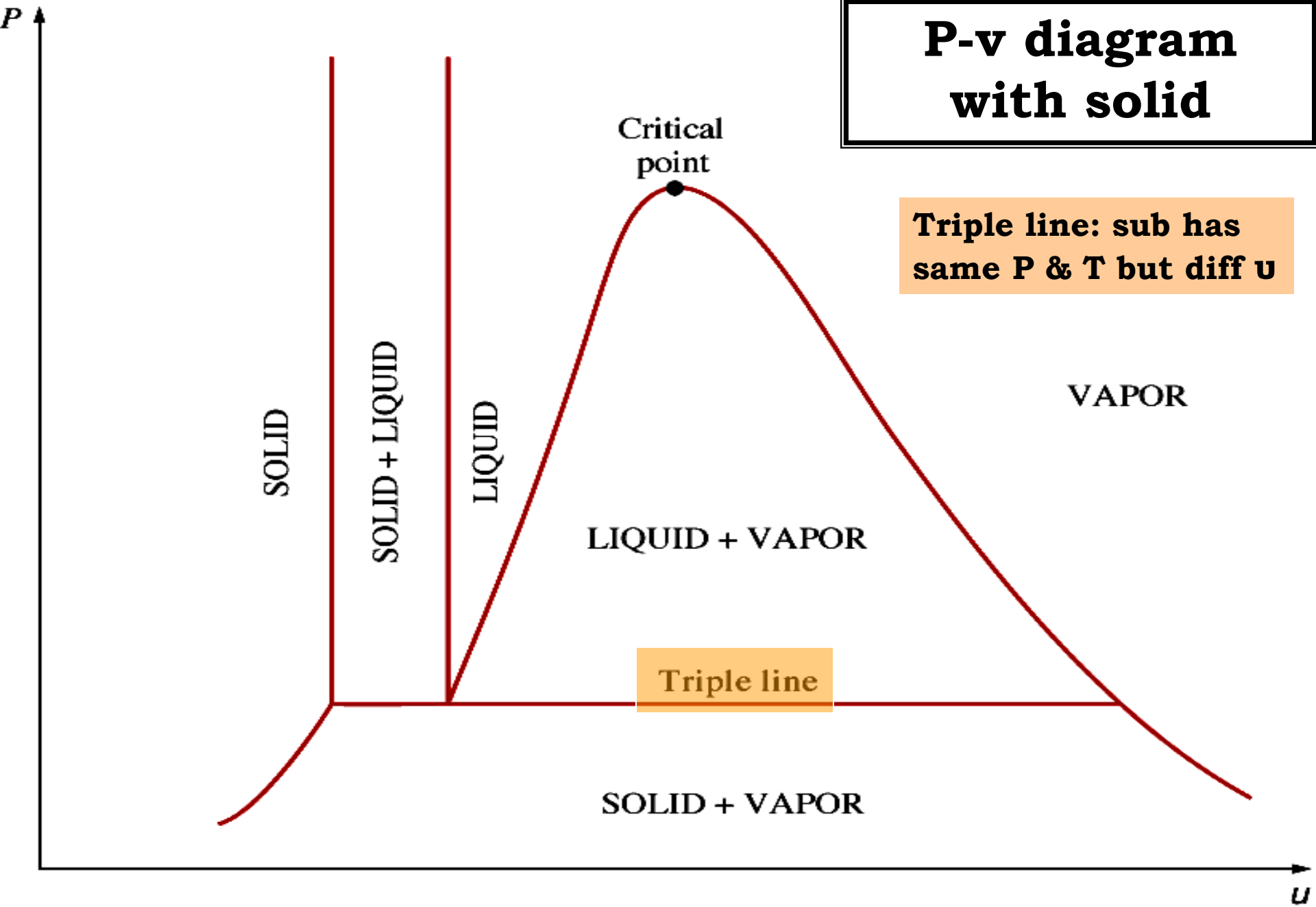

T
Critical point
COMPRESSED LIQUID REGION
Saturated liquid line
Saturated vapor line
p_2 = const. > p_1
p_1 = const.
SUPERHEATED VAPOR REGION
SATURATED LIQUID–VAPOR REGION
v

T-v diagram

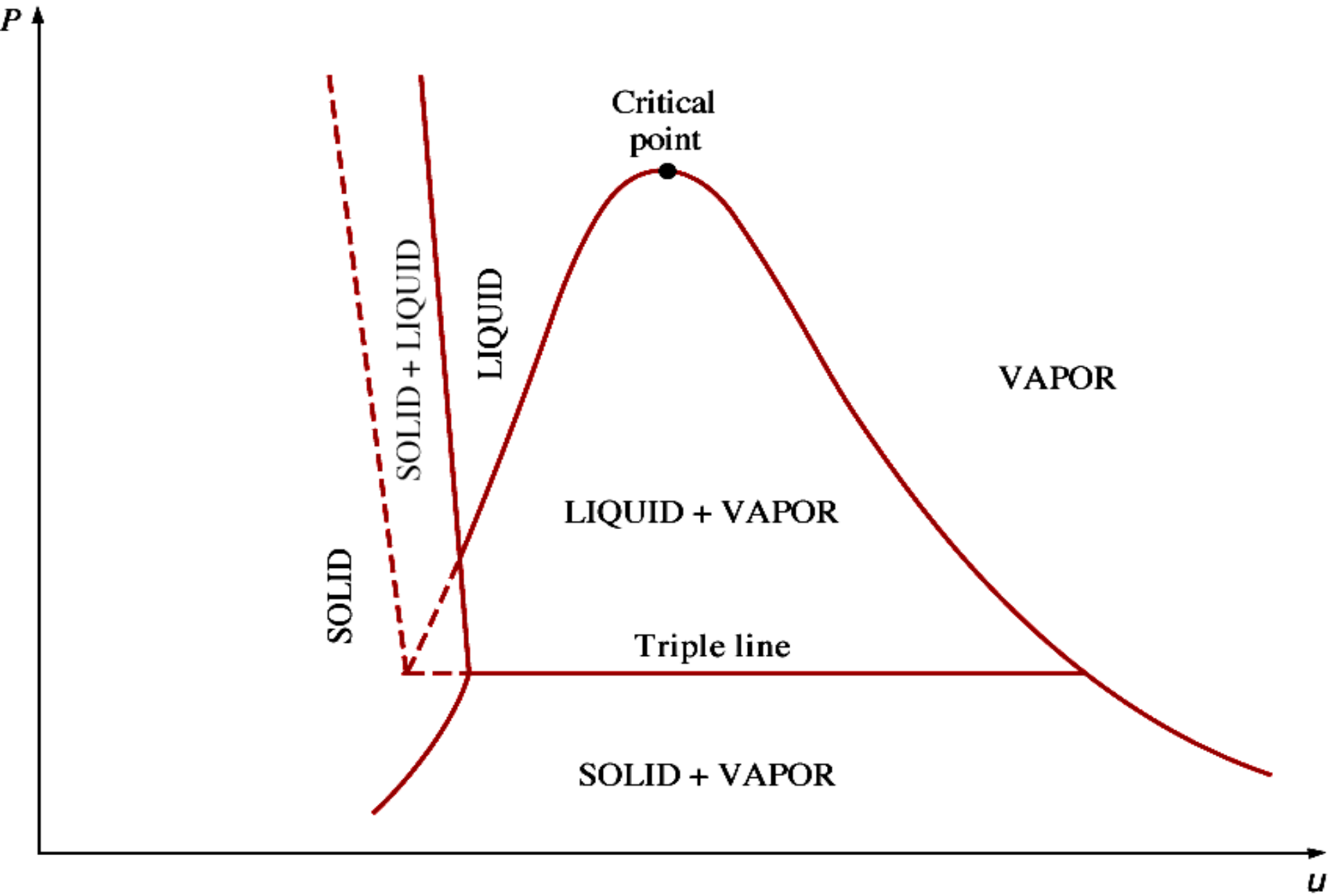

P
Critical point
Saturated liquid line
Saturated vapor line
SUPERHEATED VAPOR REGION
COMPRESSED LIQUID REGION
SATURATED LIQUID–VAPOR REGION
T_2 = const. > T_1
T_1 = const.
v

P-v diagram

P-v diagram with solid



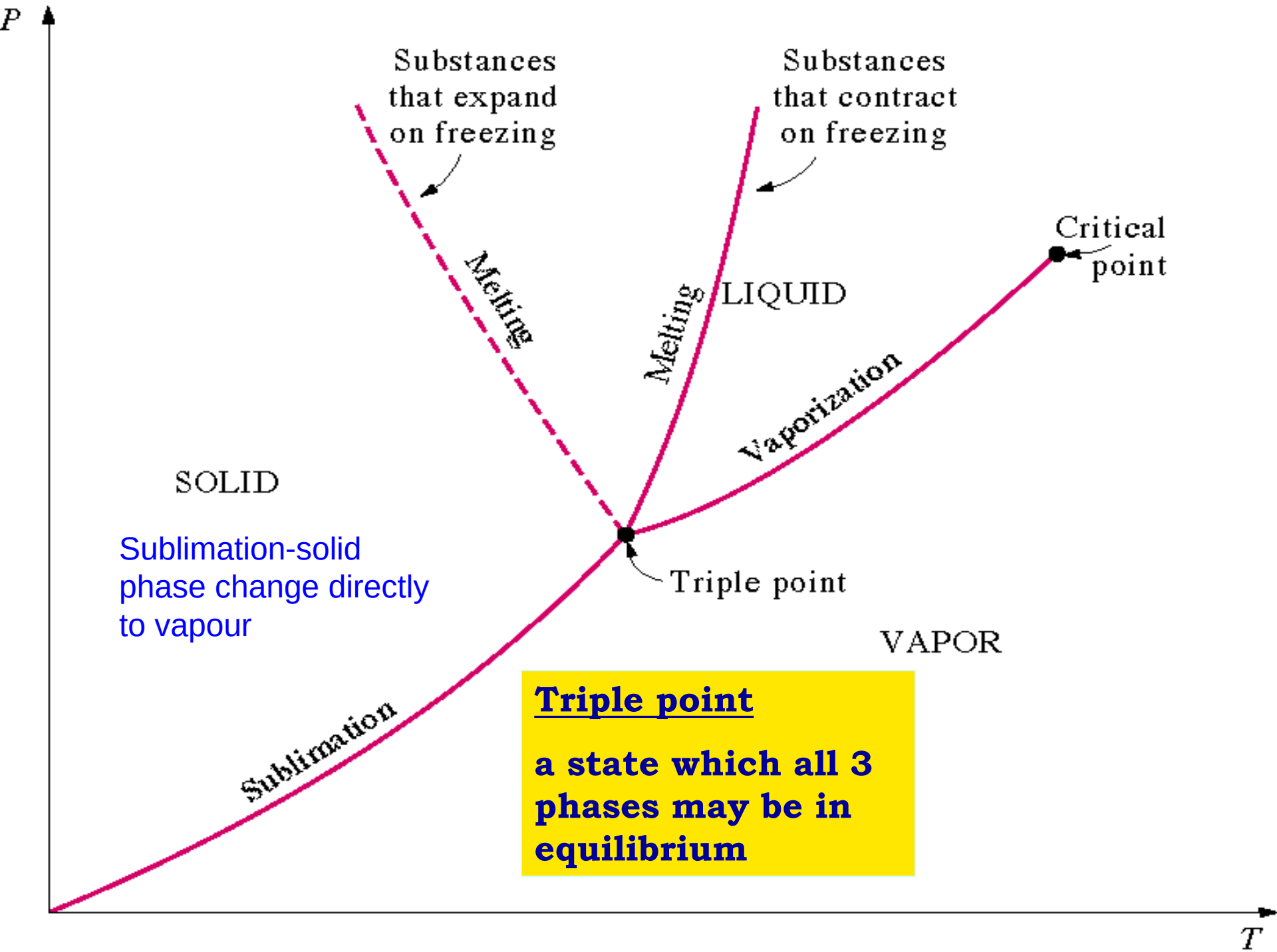
Pv Diagram of a Substance that Contracts on Freezing



Pv Diagram of a Substance that Expands on Freezing

Property Diagrams

- So far we have sketched
  - T – v diagram
  - P – v diagram
  - What about the P – T diagram?



Sublimation-solid phase change directly to vapour

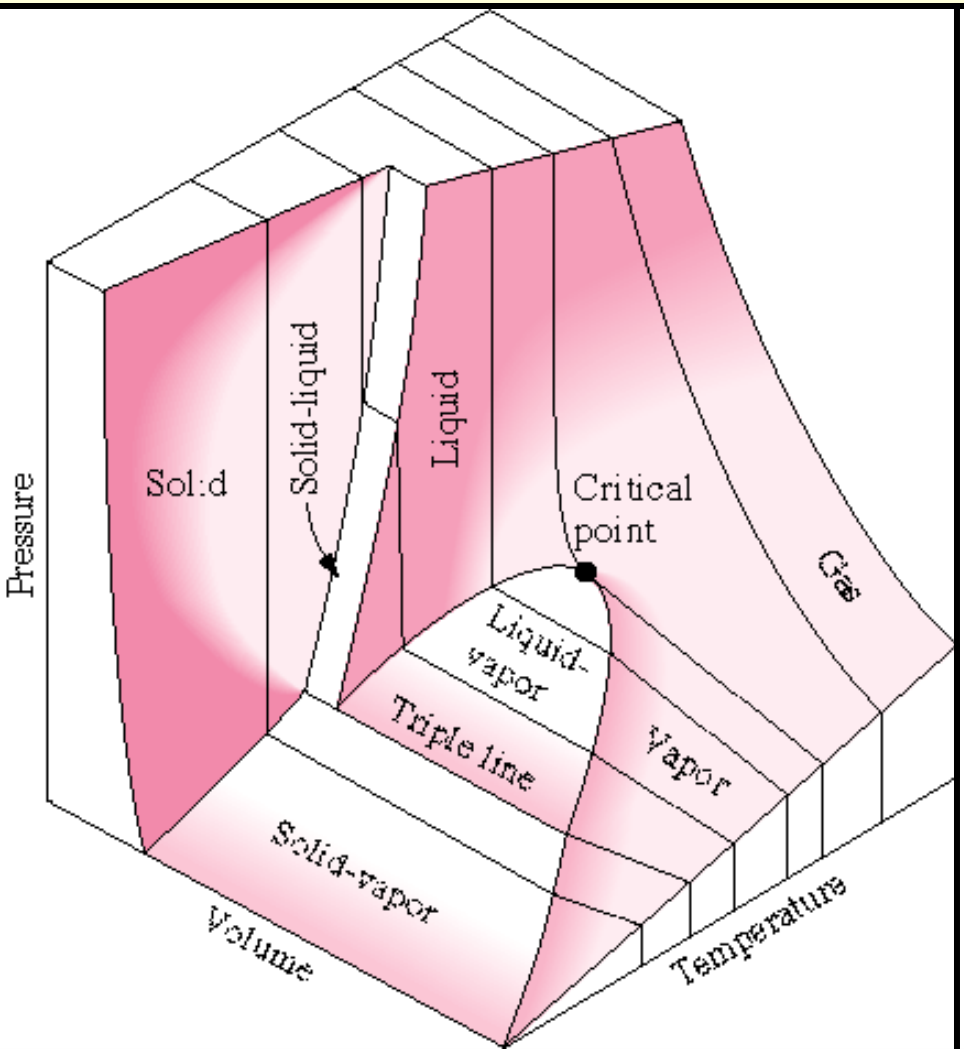
<u>Triple point</u>

a state which all 3 phases may be in equilibrium

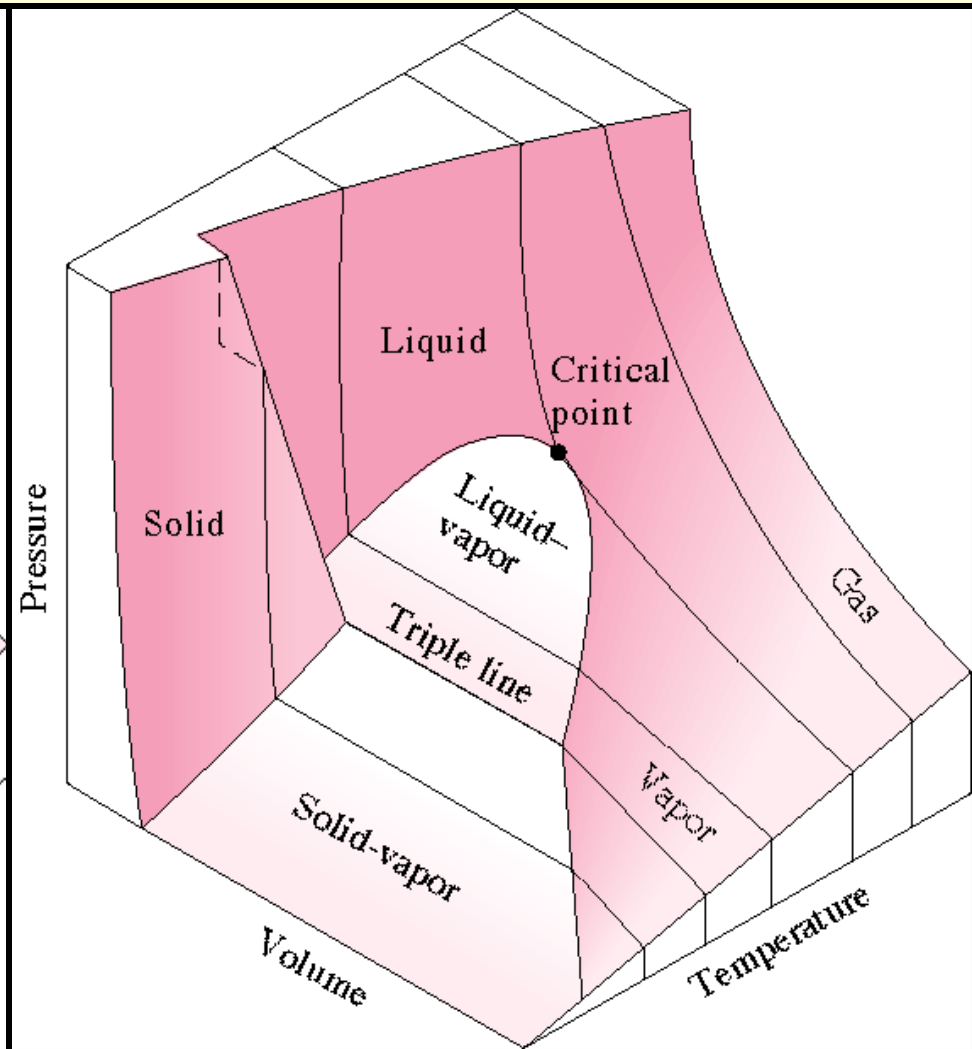
Combine all three

- You can put all three properties
  - P
  - T
  - V
- On the same diagram

Contracts on Freezing



Expands on Freezing



Property Tables (Table A-4)

P - pressure

T - temperature

u – specific volume

u – specific internal energy

h – specific enthalpy

} Chapter 5

s – specific entropy - Chapter 6

Property Tables

Table A-4

Sat.		Specific volume m^3/kg	
Temp. °C T	press kPa P_{sat}	Sat. liquid v_f	Sat. vapor v_g
85	57.83	0.001033	2.828
90	70.14	0.001036	2.361
95	84.55	0.00104	1.982

Specific temperature

Specific volume of saturated liquid

Corresponding saturation pressure

Specific volume of saturated vapor

Property Tables

Sat.		Specific volume m^3/kg	
Temp. °C T	press kPa P_{sat}	Sat. liquid v_f	Sat. vapor v_g
85	57.83	0.001033	2.828
90	70.14	0.001036	2.361
95	84.55	0.00104	1.982

Saturation Properties

- **Saturation Pressure (P_{sat}) is the pressure at which the liquid and vapor phases are in equilibrium at a given *temperature*.**

- **Saturation Temperature (T_{sat}) is the temperature at which the liquid and vapor phases are in equilibrium at a given *pressure*.**

Saturated water table

- B-1.1 or A-4
  - Saturated water temperature table
- B-1.2 or A-5
  - Saturated water pressure 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
0.01	0.6117	0.001000	206.00	0.00	2374.9	2374.9	0.00	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.02	2360.8	2381.8	21.02	2489.1	2510.1	0.0763	8.9487	9.0249
10	1.228	0.001000	106.32	42.02	2346.6	2388.7	42.02	2477.2	2519.2	0.1511	8.7488	8.8999
15	1.706	0.001001	77.885	62.98	2332.5	2395.5	62.98	2465.4	2528.3	0.2245	8.5559	8.7803
20	2.339	0.001002	57.762	83.91	2318.4	2402.3	83.91	2453.5	2537.4	0.2965	8.3696	8.6661
25	3.170	0.001003	43.340	104.83	2304.3	2409.1	104.83	2441.7	2546.5	0.3672	8.1895	8.5567
30	4.247	0.001004	32.879	125.73	2290.2	2415.9	125.74	2429.8	2555.6	0.4368	8.0152	8.4520
35	5.629	0.001006	25.205	146.63	2276.0	2422.7	146.64	2417.9	2564.6	0.5051	7.8466	8.3517
40	7.385	0.001008	19.515	167.53	2261.9	2429.4	167.53	2406.0	2573.5	0.5724	7.6832	8.2556
45	9.595	0.001010	15.251	188.43	2247.7	2436.1	188.44	2394.0	2582.4	0.6386	7.5247	8.1633
50	12.35	0.001012	12.026	209.33	2233.4	2442.7	209.34	2382.0	2591.3	0.7038	7.3710	8.0748
55	15.76	0.001015	9.5639	230.24	2219.1	2449.3	230.26	2369.8	2600.1	0.7680	7.2218	7.9898
60	19.95	0.001017	7.6670	251.16	2204.7	2455.9	251.18	2357.7	2608.8	0.8313	7.0769	7.9082
65	25.04	0.001020	6.1935	272.09	2190.3	2462.4	272.12	2345.4	2617.5	0.8937	6.9360	7.8296
70	31.20	0.001023	5.0396	293.04	2175.8	2468.9	293.07	2333.0	2626.1	0.9551	6.7989	7.7540
75	38.60	0.001026	4.1291	313.99	2161.3	2475.3	314.03	2320.6	2634.6	1.0158	6.6655	7.6812
80	47.42	0.001029	3.4053	334.97	2146.6	2481.6	335.02	2308.0	2643.0	1.0756	6.5355	7.6111
85	57.87	0.001032	2.8261	355.96	2131.9	2487.8	356.02	2295.3	2651.4	1.1346	6.4089	7.5435
90	70.18	0.001036	2.3593	376.97	2117.0	2494.0	377.04	2282.5	2659.6	1.1929	6.2853	7.4782
95	84.61	0.001040	1.9808	398.00	2102.0	2500.1	398.09	2269.6	2667.6	1.2504	6.1647	7.4151
100	101.42	0.001043	1.6720	419.06	2087.0	2506.0	419.17	2256.4	2675.6	1.3072	6.0470	7.3542
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
360	18666	0.001895	0.006950	1726.16	625.7	2351.9	1761.53	720.1	2481.6	3.9165	1.1373	5.0537
365	19822	0.002015	0.006009	1777.22	526.4	2303.6	1817.16	605.5	2422.7	4.0004	0.9489	4.9493
370	21044	0.002217	0.004953	1844.53	385.6	2230.1	1891.19	443.1	2334.3	4.1119	0.6890	4.8009
373.95	22064	0.003106	0.003106	2015.8	0	2015.8	2084.3	0	2084.3	4.4070	0	4.4070

TABLE A-5
Saturated water-Tempt table

Press. P kPa	Sat. Temp., T_{sat} °C	*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
0.6117	0.01	0.001000	206.00	0.00	2374.9	2374.9	0.00	2500.9	2500.9	0.0000	9.1556	9.1556
1.0	6.97	0.001000	129.19	29.30	2355.2	2384.5	29.30	2484.4	2513.7	0.1059	8.8690	8.9749
1.5	13.02	0.001001	87.964	54.69	2338.1	2392.8	54.69	2470.1	2524.7	0.1956	8.6314	8.8270
2.0	17.50	0.001001	66.990	73.43	2325.5	2398.9	73.43	2459.5	2532.9	0.2606	8.4621	8.7227
2.5	21.08	0.001002	54.242	88.42	2315.4	2403.8	88.42	2451.0	2539.4	0.3118	8.3302	8.6421
3.0	24.08	0.001003	45.654	100.98	2306.9	2407.9	100.98	2443.9	2544.8	0.3543	8.2222	8.5765
4.0	28.96	0.001004	34.791	121.39	2293.1	2414.5	121.39	2432.3	2553.7	0.4224	8.0510	8.4734
5.0	32.87	0.001005	28.185	137.75	2282.1	2419.8	137.75	2423.0	2560.7	0.4762	7.9176	8.3938
7.5	40.29	0.001008	19.233	168.74	2261.1	2429.8	168.75	2405.3	2574.0	0.5763	7.6738	8.2501
10	45.81	0.001010	14.670	191.79	2245.4	2437.2	191.81	2392.1	2583.9	0.6492	7.4996	8.1488
15	53.97	0.001014	10.020	225.93	2222.1	2448.0	225.94	2372.3	2598.3	0.7549	7.2522	8.0071
20	60.06	0.001017	7.6481	251.40	2204.6	2456.0	251.42	2357.5	2608.9	0.8320	7.0752	7.9073
25	64.96	0.001020	6.2034	271.93	2190.4	2462.4	271.96	2345.5	2617.5	0.8932	6.9370	7.8302
30	69.09	0.001022	5.2287	289.24	2178.5	2467.7	289.27	2335.3	2624.6	0.9441	6.8234	7.7675
40	75.86	0.001026	3.9933	317.58	2158.8	2476.3	317.62	2318.4	2636.1	1.0261	6.6430	7.6691
50	81.32	0.001030	3.2403	340.49	2142.7	2483.2	340.54	2304.7	2645.2	1.0912	6.5019	7.5931
75	91.76	0.001037	2.2172	384.36	2111.8	2496.1	384.44	2278.0	2662.4	1.2132	6.2426	7.4558
100	99.61	0.001043	1.6941	417.40	2088.2	2505.6	417.51	2257.5	2675.0	1.3028	6.0562	7.3589
125	105.97	0.001048	1.3750	444.23	2068.8	2513.0	444.36	2240.6	2684.9	1.3741	5.9100	7.2841
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
20,000	365.75	0.002038	0.005862	1785.84	509.0	2294.8	1826.59	585.5	2412.1	4.0146	0.9164	4.9310
21,000	369.83	0.002207	0.004994	1841.62	391.9	2233.5	1887.97	450.4	2338.4	4.1071	0.7005	4.8076
22,000	373.71	0.002703	0.003644	1951.65	140.8	2092.4	2011.12	161.5	2172.6	4.2942	0.2496	4.5439
22,064	373.95	0.003106	0.003106	2015.8	0	2015.8	2084.3	0	2084.3	4.4070	0	4.4070

$$u_{fg} = u_g - u_f$$

$$h_{fg} = h_g - h_f$$

$$s_{fg} = s_g - s_f$$

g stands for gas

f stands for fluid

fg stands for the difference between gas and fluid

How do we identify whether the substance is liquid or gas phase??

e.g. water at 120°C

(Table A-4 vs A-6 vs. A-7)

Determination of Phases (Liquid or Vapor)

Temperature and Pressure	Phase
If $T > T_c$	Gas (or vapor)
If $T < T_c$ and $P > P_c$	Liquid
If $T < T_c$ and $P < P_c$, check T_{sat} and P_{sat}	
• If $T > T_{sat}$ or $P < P_{sat}$	Gas (vapor)
• If $T < T_{sat}$ or $P > P_{sat}$	Liquid
• If $T = T_{sat}$ or $P = P_{sat}$	Saturated liquid-vapor
If $T < T_{triple}$	Gas or solid

Determination of Phases (Liquid or vapor)

Specific volume, ν can also be used

$\nu_f < \nu < \nu_g$ → **saturated (2 phase)**

$\nu < \nu_f$ → **compressible liquid**

$\nu_g < \nu$ → **superheated vapor**

EXERCISES

Lets try out Quiz 1

Quality, x

Fig 3-34

The relative amounts of liquid and vapor phases in a saturated mixture

$$x = \frac{mass_{saturated\ vapor}}{mass_{total}} = \frac{m_g}{m_f + m_g}$$

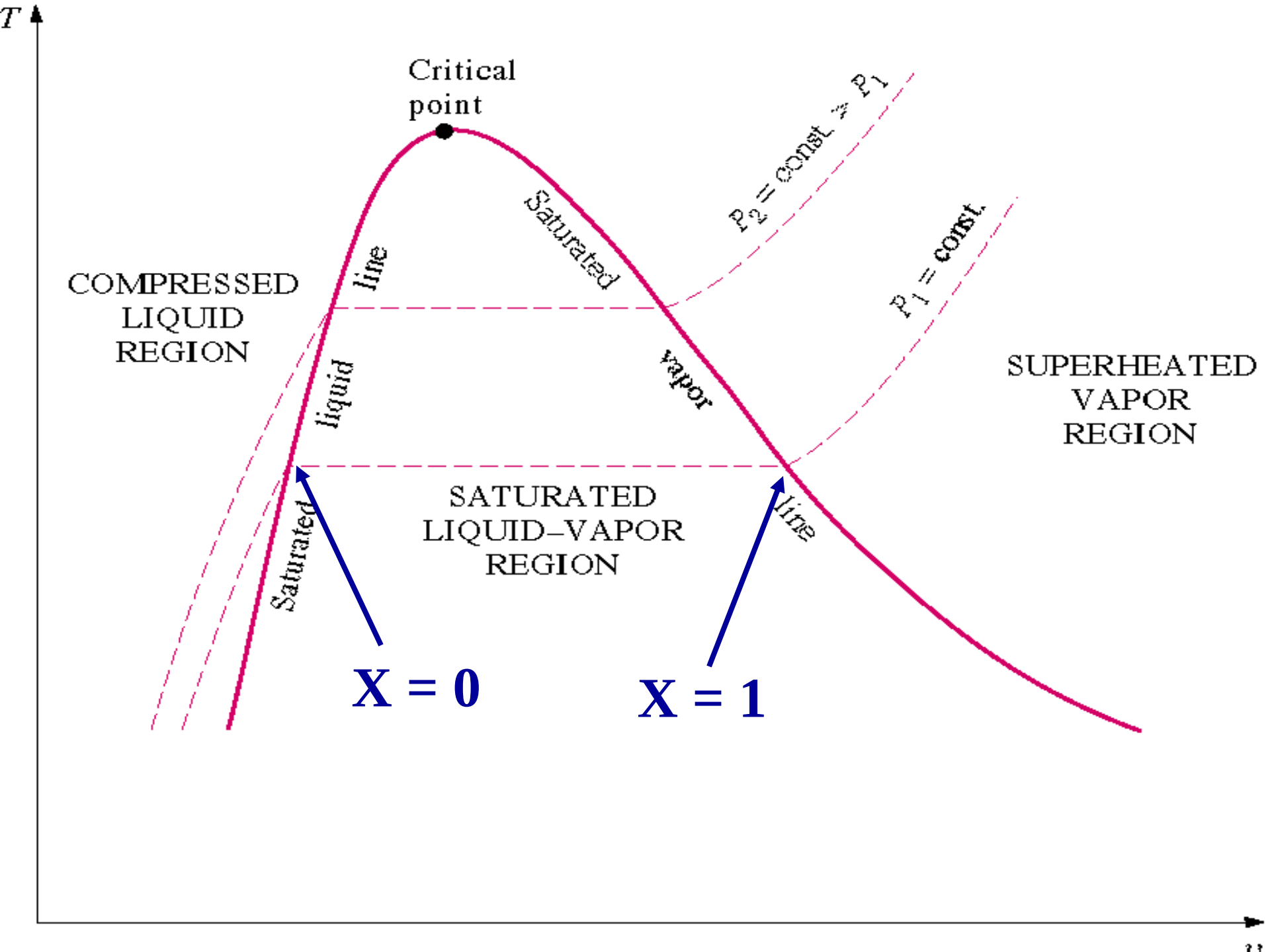
Quality, x

$$x = \frac{mass_{saturated\ vapor}}{mass_{total}} = \frac{m_g}{m_f + m_g}$$

x = 0 the material is all saturated liquid

x = 1 the material is all saturated gas

x is not meaningful when you are out of the saturation region


T
Critical point
Saturated liquid line
Saturated vapor line
P_2 = const > P_1
P_1 = const.
COMPRESSED LIQUID REGION
SUPERHEATED VAPOR REGION
SATURATED LIQUID–VAPOR REGION
X = 0
X = 1

Average Properties

$$y = y_f + x(y_g - y_f)$$
$$= y_f + \cancelto{0}{x}\,y_{fg} = y_g$$

When x = 0 we have all liquid, and $y = y_f$

When x = 1 we have all gas, and $y = y_f + y_{fg} = y_g$

When x is not given, we can find x by using the relation

$$x = \frac{y - y_f}{y_{fg}}$$

TABLE A-6 Superheated water

T °C	v m^3/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	P = 0.01 MPa (45.81°C)			
Sat.	14.670	2437.2	2583.9	8.1488
50	14.867	2443.3	2592.0	8.1741
100	17.196	2515.5	2687.5	8.4489
150	19.513	2587.9	2783.0	8.6893
200	21.826	2661.4	2879.6	8.9049
250	24.136	2736.1	2977.5	9.1015
300	26.446	2812.3	3076.7	9.2827
400	31.063	2969.3	3280.0	9.6094
500	35.680	3132.9	3489.7	9.8998
600	40.296	3303.3	3706.3	10.1631
700	44.911	3480.8	3929.9	10.4056
800	49.527	3665.4	4160.6	10.6312
900	54.143	3856.9	4398.3	10.8429
1000	58.758	4055.3	4642.8	11.0429
1100	63.373	4260.0	4893.8	11.2326
1200	67.989	4470.9	5150.8	11.4132
1300	72.604	4687.4	5413.4	11.5857

T °C	v m^3/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	P = 0.05 MPa (81.32°C)			
Sat.	3.2403	2483.2	2645.2	7.5931
100	3.4187	2511.5	2682.4	7.6953
150	3.8897	2585.7	2780.2	7.9413
200	4.3562	2660.0	2877.8	8.1592
250	4.8206	2735.1	2976.2	8.3568
300	5.2841	2811.6	3075.8	8.5387
400	6.2094	2968.9	3279.3	8.8659
500	7.1338	3132.6	3489.3	9.1566
600	8.0577	3303.1	3706.0	9.4201
700	8.9813	3480.6	3929.7	9.6626
800	9.9047	3665.2	4160.4	9.8883
900	10.828	3856.8	4398.2	10.1000
1000	11.751	4055.2	4642.7	10.3000
1100	12.675	4259.9	4893.7	10.4897
1200	13.598	4470.8	5150.7	10.6704
1300	14.521	4687.3	5413.3	10.8429

TABLE A-7 Compressed liquid water

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	P = 5 MPa (263.94°C)			
Sat.	0.0012862	1148.1	1154.5	2.9207
0	0.0009977	0.04	5.03	0.0001
20	0.0009996	83.61	88.61	0.2954
40	0.0010057	166.92	171.95	0.5705
60	0.0010149	250.29	255.36	0.8287
80	0.0010267	333.82	338.96	1.0723
100	0.0010410	417.65	422.85	1.3034
120	0.0010576	501.91	507.19	1.5236
140	0.0010769	586.80	592.18	1.7344
160	0.0010988	672.55	678.04	1.9374
180	0.0011240	759.47	765.09	2.1338
200	0.0011531	847.92	853.68	2.3251
220	0.0011868	938.39	944.32	2.5127
240	0.0012268	1031.6	1037.7	2.6983
260	0.0012755	1128.5	1134.9	2.8841

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	P = 10 MPa (311.00°C)			
Sat.	0.0014522	1393.3	1407.9	3.3603
0	0.0009952	0.12	10.07	0.0003
20	0.0009973	83.31	93.28	0.2943
40	0.0010035	166.33	176.37	0.5685
60	0.0010127	249.43	259.55	0.8260
80	0.0010244	332.69	342.94	1.0691
100	0.0010385	416.23	426.62	1.2996
120	0.0010549	500.18	510.73	1.5191
140	0.0010738	584.72	595.45	1.7293
160	0.0010954	670.06	681.01	1.9316
180	0.0011200	756.48	767.68	2.1271
200	0.0011482	844.32	855.80	2.3174
220	0.0011809	934.01	945.82	2.5037
240	0.0012192	1026.2	1038.3	2.6876
260	0.0012653	1121.6	1134.3	2.8710
280	0.0013226	1221.8	1235.0	3.0565
300	0.0013980	1329.4	1343.3	3.2488

Linear Interpolation

Tutorial problem 5b

A	B
100	5
130	X
200	10

$$\frac{130-100}{200-100}=\frac{x-5}{10-5}$$

Exercises 1

Determine the quality (if saturated) or temperature (if superheated) of water at the given two states;

i) $120^{o}C$, 1 m^3/kg

ii) 10 MPa, 0.01 m^3/kg

Exercises

Quiz 4

Quiz 5

Quiz 6

Quiz 7

POP QUIZ 2

Open BOOK

Individual

NO discussion

15 minutes

Equations of State

Any relation among the pressure (P), temperature (T) and specific volume (v) of a substance is called an equation of state

$$PV = RT$$

Equations vs Tables

- The behavior of many gases (like steam) is not easy to predict with an equation
- That's why we have tabulated tables
- Other gases (like air) follow the ideal gas law – we can calculate their properties

Ideal Gas Law

- **PV=nRT**
  - **Used in your Chemistry class**
  - **From now on we will refer to the gas constant , R, as the universal gas constant, R_u , and redefine R=** $\frac{R_u}{MW}$
- **PV=mRT**
  - **R is different for every gas**
  - **Tabulated in the back of the book (Table A-2)**

Ideal Gas Law

- $v = V/m$
- $Pv = RT$
  - This is the form we will use the most
  - R = ??? → refer notes conversion unit

When does the ideal gas law apply?

The ideal gas equation of state can be derived from basic principles if one assumes:

1. Intermolecular forces are small
2. Volume occupied by the particles is small

These assumptions are true when the molecules are far apart

Criteria

- **The ideal gas law applies when the pressure is low, and the temperature is high - compared to the critical values**

$P \ll P_c$	**ideal gas assumption is accurate (regardless of temperature)**
$T \gg 2T_c$	**ideal gas assumption is accurate for $P < 4P_c$**
$T \ll 2T_c$ and P is not to low	**→ ideal gas assumption is not valid**

EXERCISE

Lets try Quiz 12

Compressibility Factor, z

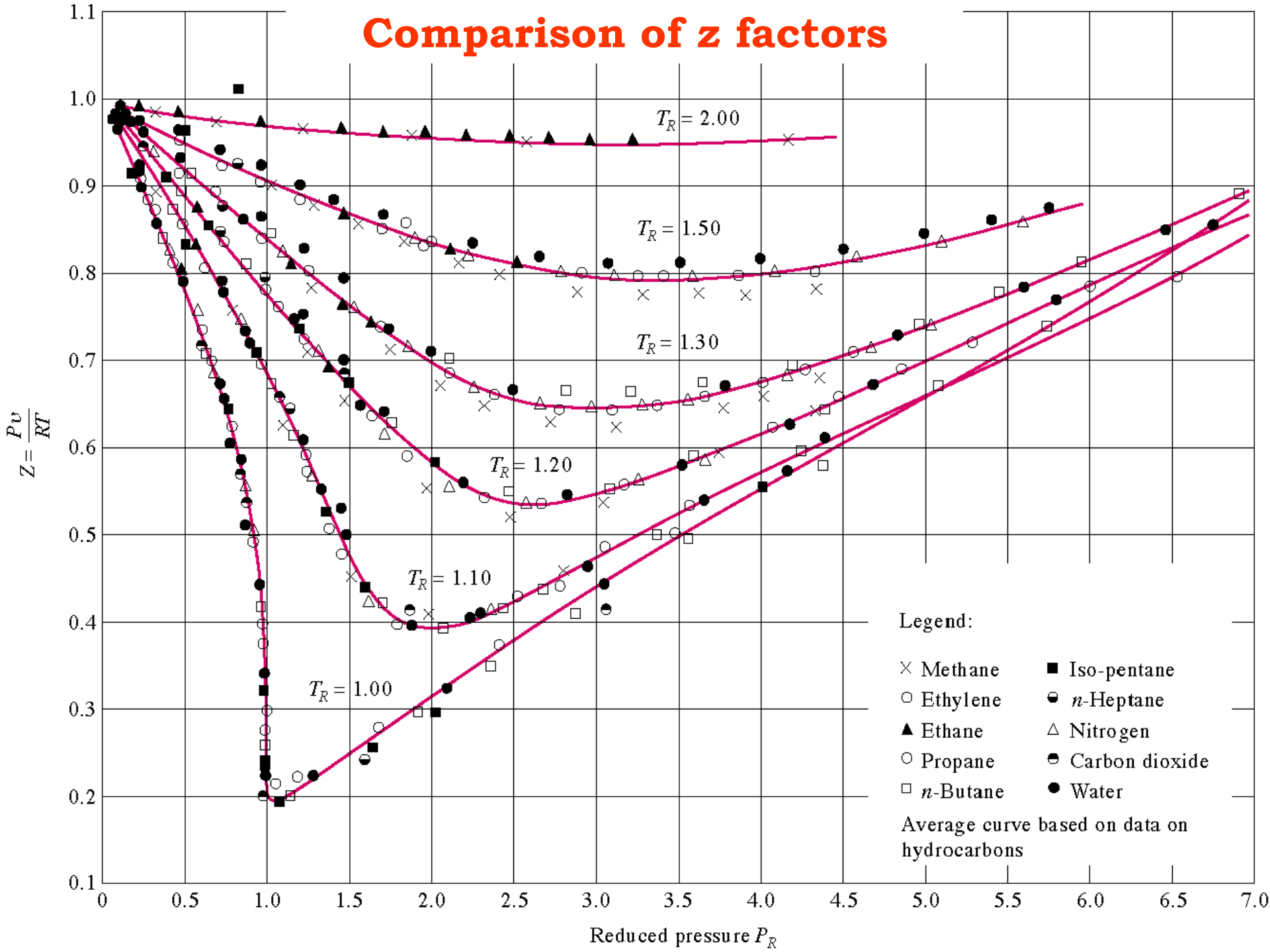
- You can adjust the ideal gas law with a fudge factor, called the compressibility factor
- $Pv = z\,RT$
- z is just a value you put in to make it work out (fig A-15 pg 908)
- $z = 1$ for ideal gases

Principle of Corresponding States

- The *Z* factor is approximately the same for all gases at the same **reduced temperature** and **reduced pressure**

$$T_R = \frac{T}{T_{cr}} \quad \text{and} \quad P_R = \frac{P}{P_{cr}}$$

Comparison of z factors



Calculating V from Z

$$Z = \frac{V_{actual}}{V_{ideal}}$$

$$V_a = ZV_i$$

Combined Gas Law

$$\frac{P_1V_1}{RT_1} = \frac{P_2V_2}{RT_2}$$

EXERCISE

Lets try Quiz 13

Determine the specific volume of superheated water vapor at 10 MPa and 400°C using

a) The ideal-gas equation
b) The generalized compressibility chart
c) The steam tables

Summary

- Today we talked about how to describe the state of a substance with thermodynamic properties
- We learned how to use the property tables
- We introduced equations of state

MORE EXERCISE

Quiz 2

Quiz 3

Quiz 8

Quiz 9

Quiz 10

Quiz 11