CHAPTER

2

Properties of Pure Substances

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A Pure Substance

Is a substance that is chemically homogenous and fixed in chemical composition.(e.g. water, nitrogen, air & etc.)

→ **mixture of oil and water is not a pure substance.**

→ **a mixture of two or more phases of a pure substance is still a pure substance.**

Phase of a Pure Substance

The phase of a substance is the homogeneous, chemical, and physical of aggregation of its molecules.

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The molecules in a <u>solid</u> are kept at their positions by the large spring like inter-molecular forces.

At high temperature, molecules overcome the inter molecules forces and break away.

In the <u>liquid</u> phase the molecules are no longer at fixed positions, and chunks of the molecules float about each other.

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In the gas phase the molecules are far apart from each other, irregular and move about at random colliding with each other. Molecules are higher energy level than they are in liquid or solid phases.

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Phase Change of Pure Substances

Attention will be focused on liquid and vapor phases in this section. All substances exhibit general behavior. Water will be used in the following example.

compressed liquid or subcooled liquid

At 1 atm and 20°C, water exists in the liquid phase(i.e. not about to vaporize).

As heat added the temperature increases and water expands.(i.e. v increases)

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Saturated liquid

At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize.

Any addition of heat will cause the phase change.

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Saturated liquid–vapor mixture

The state at which the liquid and vapor phases coexist in equilibrium.

Once boiling starts, the temperature will not rise until the liquid completely vaporizes.

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Saturated vapor

A vapor that is *about to condense.*

Superheated vapor

A vapor that is *not about to condense* (i.e., not a saturated vapor).

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FIGURE 2-1

***T-v* diagram for the heating process of water at constant pressure.**

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FIGURE 2-2 Liquid-vapor saturation curve

Holding the pressure constanta t 1 atm, boiling takes place at 100°C. By changing the pressure we can change the boiling temperature of water.

Saturation temperature T_{sat}

The temperature at which a pure substance starts boiling.

Saturation pressure P_{sat}

The pressure at which a pure substance starts boiling.

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Property Diagrams for phase-Change Processes

FIGURE 2-3 **T-V Diagram of a Pure Substance**

Critical point

The point at which the saturated liquid and saturated vapor states are identical.

T_c is the maximum temperature at which liquid and vapor phases can co-exist in equilibrium.

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FIGURE 2-4
***P-v* diagram of a pure substance.**

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FIGURE 2-5

***T-v* diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).**

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FIGURE 2-6

***P-v* diagram of a substance that contracts on freezing.**

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FIGURE 2-7
***P-v* diagram of a substance that expands on freezing (such as water).**

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When all three phases of a substance co-exist in equilibrium under some conditions, it is called <u>triple phase</u>.

On P-v or T-v diagrams → Triple line

On P-T or T-v diagrams → Triple point

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FIGURE 2-8
***P-T* diagram of pure substances.**

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FIGURE 2-9
***P-v-T* surface of a substance that *contracts* on freezing.**

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FIGURE 2-10
***P-v-T* surface of a substance that *expands* on freezing (like water).**

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PROPERTY TABLES

Enthalpy $\longrightarrow H = U + PV$ (kJ) **or** $h = u + Pv$ (kJ/kg)

If u is not listed $\longrightarrow$ u= h - Pv

Saturated Liquid and Saturated Vapor States

(table A4 and A5 in cengel)

Subscripts

f – saturated liquid

g – saturated vapor

fg – the difference between saturated vapor and saturated liquid

e.g., v_f **= specific volume of saturated liquid**

v_g **= specific volumee of saturated vapor**

$$v_{fg} = v_g - v_f$$

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FIGURE 2-11
A partial list of Table A–4.

Temp. °C T	Sat. press kPa P_{sat}	Specific volume m^3/kg Sat. liquid v_f	Sat. vapor v_g
85	57.83	0.001 033	2.828
90	70.14	0.001 036	2.361
95	84.55	0.001 040	1.982

Specific temperature

Corresponding saturation pressure

Specific volume of saturated liquid

Specific volume of saturated vapor

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Saturated Liquid–Vapor Mixture

In order to know the properties of the liquid and vapor phase in the mixture a new property is defined:

Quality, x : The ratio of the mass of vapor to the total mass of the mixture.
Quality is between 0 and 1 0: sat. liquid, 1: sat. vapor.

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}} \qquad m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$

$$V = V_f + V_g$$

$$V = mv \rightarrow m_t v_{av} = m_f v_f + m_g v_g$$

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

$$\div m_t \rightarrow \quad v_{av} = (1 - x) v_f + x v_g$$

or $\quad v_{av} = v_f + x v_{fg} \qquad x = \dfrac{v_{av} - v_f}{v_{fg}}$

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Similar equations can be derived for u or h:

$$u_{\text{avg}} = u_f + xu_{fg} \qquad (\text{kJ/kg})$$

$$h_{\text{avg}} = h_f + xh_{fg} \qquad (\text{kJ/kg})$$

Example **5 kg of steam at 200kPa occupied a volume of 2.60 m^3 . Determine temperature and quality.**

$$v_{av} \rightarrow v = \frac{volume}{mass} = \frac{2.60}{5} = 0.52\, {}^{m^3}/_{kg}$$

Compare this with the values given in Table A-5

Note : T_{sat}=120.23 ºC at 200 kPa (=0.200 Mpa)

v_f =0.001061 and v_g =0.8857

$$x = \frac{v_{av} - v_f}{v_{fg}} = \frac{v - v_f}{v_g - v_f} = \frac{0.52 - 0.001061}{0.8857 - 0.001061} = 0.587$$

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FIGURE 2-12
A partial listing of Table A–6.

T, °C	v, m³/kg	u, kJ/kg	h, kJ/kg
	$P = 0.1$ MPa (99.63°C)		
Sat.	1.6940	2506.1	2675.5
100	1.6958	2506.7	2676.2
150	1.9364	2582.8	2776.4
⋮	⋮	⋮	⋮
1300	7.260	4683.5	5409.5
	$P = 0.5$ MPa (151.86°C)		
Sat.	0.3749	2561.2	2748.7
200	0.4249	2642.9	2855.4
250	0.4744	2723.5	2960.7

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Superheated Vapor (Table A-6)

characterized by

Lower pressures ($P < P_{sat}$ at a given T)
Higher tempreatures ($T > T_{sat}$ at a given P)
Higher specific volumes ($v > v_g$ at a given P or T)
Higher internal energies ($u > u_g$ at a given P or T)
Higher enthalpies ($h > h_g$ at a given P or T)

Example

$$at\ 0.5\ MPa \rightarrow h_g = 2748.7\ {}^{kJ}/_{kg}$$

$$T_{sat} = 151.86\ {}^{o}C$$

However at the same pressure,
if T= 200 ºC → h= 2855.4 $^{kJ}/_{kg}$

$$\rightarrow h > h_g$$

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Compressed Liquid

characterized by

Higher pressures ($P > P_{sat}$ at a given T)
Lower tempreatures ($T < T_{sat}$ at a given P)
Lower specific volumes ($v < v_f$ at a given P or T)
Lower internal energies ($u < u_f$ at a given P or T)
Lower enthalpies ($h < h_f$ at a given P or T)

In the absence of data a compressed liquid is approximated as a saturated liquid at the given temperature.

Given: P and T

$$v \cong v_{f\,@T}$$
$$u \cong u_{f\,@T}$$
$$h \cong h_{f\,@T}$$

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Example

at 80 °C $P_{sat} = 47.39\ kPa$

If our pressure is 5 MPa then we have compressed liquid.

For compressed liquid table(A-7):

$$\left.\begin{array}{l} P = 5\ MPa \\ T = 80°C \end{array}\right\} \quad u = 333.72\ {}^{kJ}/_{kg}$$

From the saturation table(A-4):

$$u_f = 334.86\ {}^{kJ}/_{kg}$$

If we make $u \cong u_{f@80°C}$,the error is:

$$\frac{334.86 - 333.72}{333.72} = 0.0034(0.34\%)$$

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Example

State	1	2	3	4	5
P,kPa	200	300	2000	0.476	5000
T, ºC	120.23	133.56	300	150	100
x, %	80	I	M	92	M
v, m^3/kg	0.709	I	0.125	0.361	0.00104

$$state\ 1(table\ A-5) \rightarrow T = T_{sat@200kPa} = 120.23°C$$

$$v = v_f + xv_{fg}$$

= 0.001061+ 0.8(0.8857-0.001061)=0.709

$$state\ 2 \rightarrow at\ 300\ kPa\ \ T_{sat} = 133.55°C$$

,either saturated liquid
or saturated vapor
or saturated liquid-vapor mixture

X=indeterminate=I
V=indeterminate=I

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$$state\ 3 \rightarrow at\ 2000\ kPa\ \ T_{sat} = 212.42°C$$

$$\therefore Superheated(\ Table\ A-6)$$

x=meaning less=M

v=012547 m^3/kg

$$state\ 4 \rightarrow at\ 150°C\ \ P_{sat} = 0.4758MPa\ \ v_f = 0.001091 \qquad v_g = 0.3928\ m^3/kg$$

$$x = \frac{v - v_f}{v_g - v_f} = \frac{0.361 - 0.001091}{0.3928 - 0.001091} = 0.919(or\ 92\%)$$

$$state\ 5 \rightarrow at\ 5000kPa\ \ T_{sat} = 263.99°C \xrightarrow{\text{Compressed liquid}}$$

x=meaningless=M

$$Table\ (A-7)\ at\ 5MPa\ and\ 100°C \qquad v = 0.001041\ m^3/kg$$

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The Ideal Gas Equation of State

<u>Equation of State:</u> any equation that relates the pressure, temperature, and specific of a substance.

Specific volume

Ideal-gas equation of state $\longrightarrow$ $P = R\left(\frac{T}{v}\right)$ or $Pv = RT$

Absolute temperature

Absolute pressure **Gas constant**

Ideal gas $\longrightarrow$ **is a gas which obeys the above relation. The gas R is different for each gas.**

$$R = \frac{R_u}{M} \; {}^{kJ}/_{kg.K}$$

R_u **=universal gas constant**

M=molar mass(molecules weight)

R_u **= 8.314** ${}^{kJ}/_{(kmol.K)}$ **or 1.986** ${}^{Btu}/_{(lbmol.R)}$ **(same for all substances)**

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$$m = MN \qquad (\text{kg})$$

m → Mass of system

N → Mole number

Ideal Gas Equation in different forms:

$$V = mv \longrightarrow PV = mRT$$

$$mR = (MN)R = NR_u \longrightarrow PV = NR_uT$$

$$V = N\bar{v} \longrightarrow P\bar{v} = R_uT$$

$\bar{v}$ → Molar specific volume

State 1

$$\rightarrow \boldsymbol{P_1V_1 = m\,RT_1}$$

State 2

$$\boldsymbol{P_2V_2 = m\,RT_2}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \text{mR}$$

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Example

Determine the density and specific volume of air at room temperature.

$\rightarrow PV = m\,RT$ **or** $P\,{}^{1}/_{\rho} = RT$

Room temperature=20ºC
273+20=293K

$$\rho = \frac{P}{RT} = \frac{101\,(kPa)}{0.287\left({}^{kJ}/_{kg}\right)293\,(K)} = 1.2\ {}^{kg}/_{m^3}$$

$$v = \frac{1}{\rho} = 0.83\ {}^{m^3}/_{kg}$$

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FIGURE 2-14
Percentage of error 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.

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COMPRESSIBILITY FACTOR

Gases deviate from ideal-gas behavior significantly at state near saturation region and the critical point.
Hence a correction is introduced:

$\longrightarrow$ **compressibility factor =** $Z = \dfrac{Pv}{RT}$ **(for ideal gases Z=1)**

Z is an indication of deviation from ideal gas behavior.
Gases behave differently at a given temperature and pressure.

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

$\downarrow$

Reduced Pressure

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

$\downarrow$

Reduced Pressure

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

FIGURE 2-13
Comparison of Z factors for various gases.

1) $P_R \ll 1$, gases behave as an ideal gas regardless of T.
2) $T_R > 2$, ideal gas assumed regardless of P(except $P_R \gg 1$)
3) The deviation from ideal-gas is greatest around critical point (i.e. $T_R = 1$, $P_R = 1$)

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Example

Determine the specific volume of R-134-a at 1 MPa and 50ºC.

$\longrightarrow$ **if ideal gas equation used**

$$\rightarrow v = \frac{RT}{P} = \frac{0.08149 \times 323}{1000} = 0.02632 \quad m^3/kg$$

Z can be determined:

$$P_R = \frac{P}{P_{cr}} = \frac{1MPa}{4.067MPa} = 0.245$$

$$T_R = \frac{T}{T_{cr}} = \frac{323K}{374.3\,K} = 0.862$$

$$Z = 0.835 \rightarrow v = Zv_{ideal}$$

$$v = 0.835 \times 0.02632$$

$$= 0.02197 \quad m^3/kg$$

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FIGURE 2-19
Percentage of error involved in various equations of state for nitrogen.

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FIGURE 2-20
Ideal-gas constant-pressure specific heats for some gases (see Table A–*2c* for C_p equations).