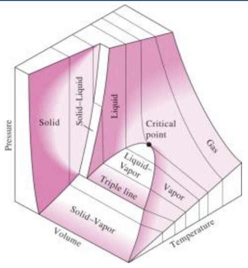
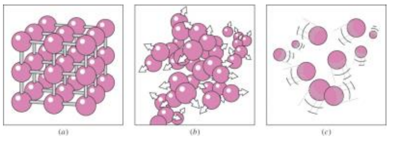
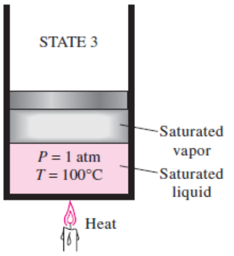
University Of Jordan
Faculty of Engineering and Technology
Department of Chemical Engineering



Thermodynamics I



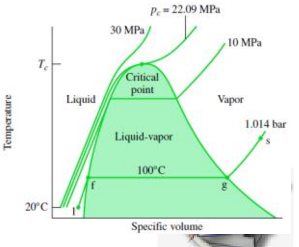


Properties of Pure Substances

Given: P and T

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

Dr.-Eng. Zayed Al-Hamamre



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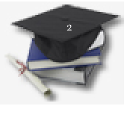
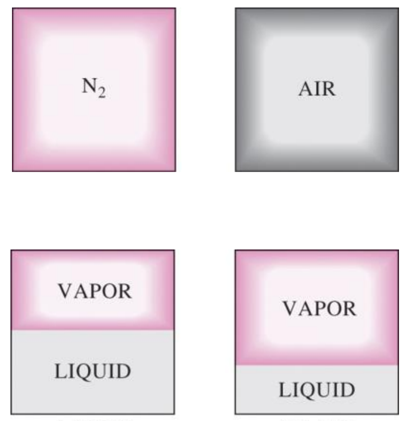
Content



Pure substance

- **pure substance** is a substance that has a fixed chemical composition throughout such as Water, nitrogen, helium, and carbon dioxide.
- A pure substance does not have to be of a single chemical element or compound,
- A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous (air).
- A mixture of oil and water is not a pure substance, since oil is not soluble in water.
- A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same (mixture of ice and liquid water).



(*a*) H_2O (*b*) AIR

Simple compressible systems

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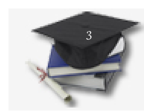
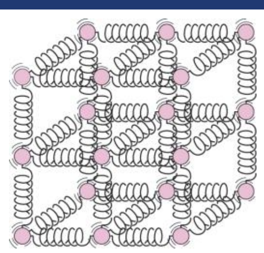
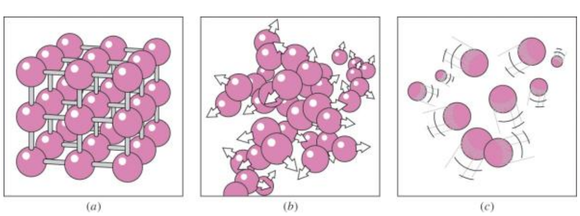


Phases of Pure substance



The molecules in a solid are kept at their positions by the large springlike inter-molecular forces.

In a solid, the attractive and repulsive forces between the molecules tend to maintain them at relatively constant distances from each other.



The arrangement of atoms in different phases: (*a*) molecules are at relatively fixed positions in a solid, (*b*) groups of molecules move about each other in the liquid phase, and (*c*) molecules move about at random in the gas phase.

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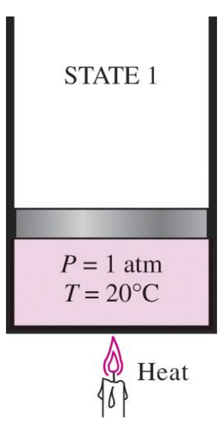
Phases of Pure substance

- A phase is identified as having a distinct molecular arrangement that is homogeneous throughout and separated from the others by easily identifiable boundary surfaces.
- A substance may have several phases within a principal phase, each with a different molecular structure

Phases change processes of pure substance

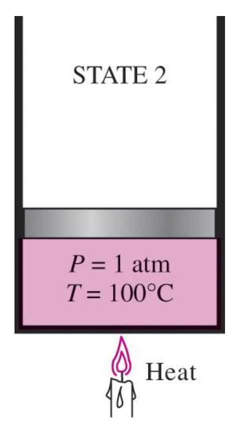
- ✓ **Compressed liquid (subcooled liquid)**: A substance that it is *not about to vaporize.*
- ✓ **Saturated liquid**: A liquid that is *about to vaporize.*

Phases Change Processes of Pure Substance



At 1 atm and 20°C, water exists in the liquid phase (***compressed liquid***).

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

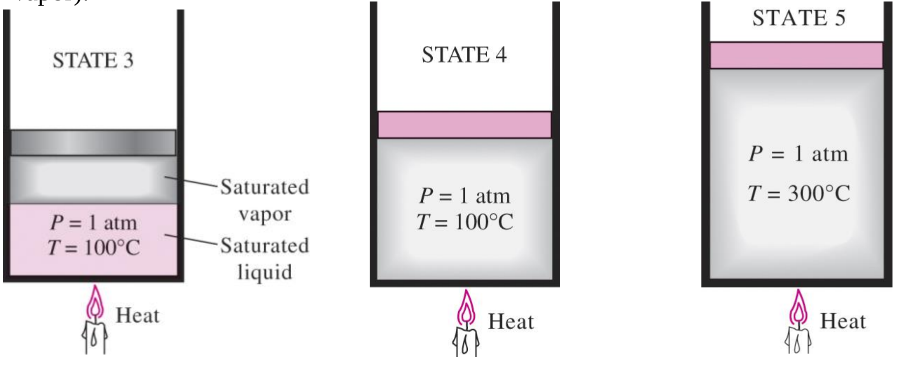


Phases Change Processes of Pure Substance

Saturated vapor: A vapor that is *about to condense.*

Saturated liquid–vapor mixture: The state at which the *liquid and vapor phases coexist* in equilibrium.

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



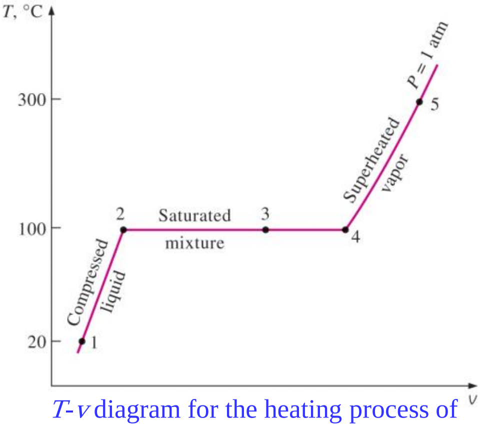
As more heat is transferred, part of the saturated liquid vaporizes (***saturated liquid–vapor mixture***).

At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (***saturated vapor***).

As more heat is transferred, the temperature of the vapor starts to rise (***superheated vapor***).

Phases Change Processes of Pure Substance

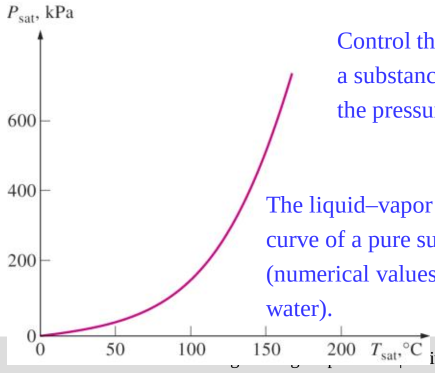
- If the entire process between state 1 and 5 described in the figure is reversed by cooling the water while maintaining the pressure at the same value, the water will go back to state 1, retracing the same path
- The amount of heat released will exactly match the amount of heat added during the heating process.



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

Saturation Temperature and Saturation Pressure

- The temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.
- Water boils at 100°C at 1 atm pressure.
- **Saturation temperature T_{sat}**: The temperature at which a pure substance changes phase at a given pressure.
- **Saturation pressure P_{sat}**: The pressure at which a pure substance changes phase at a given temperature.



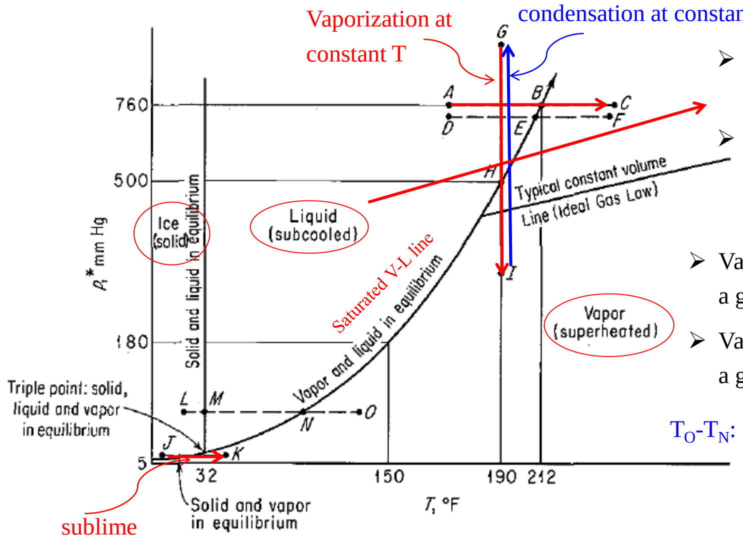
Control the boiling temperature of a substance by simply controlling the pressure,

The liquid–vapor saturation curve of a pure substance (numerical values are for water).

Saturation (boiling) pressure of water at various temperatures

Temperature, T, °C	Saturation pressure, P_{sat}, kPa
−10	0.26
−5	0.40
0	0.61
5	0.87
10	1.23
15	1.71
20	2.34
25	3.17
30	4.25
40	7.39
50	12.35
100	101.4
150	476.2
200	1555
250	3976
300	8588

Phase Diagrams

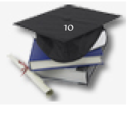


- Vapor at T < $T_{saturated}$ at a given P, or
- Vapor at P > $P_{saturated}$ at a given T.

- Vapor at T > $T_{saturated}$ at a given P, or
- Vapor at P < $P_{saturated}$ at a given T.

T_O-T_N: Degrees of superheat

T_N is $T_{saturated}$



Phases Change Processes of Pure Substance

- ✓ **Latent heat**: The amount of energy absorbed or released during a phase-change process.
- ✓ **Latent heat of fusion**: The amount of energy absorbed during melting. It is equivalent to the amount of energy released during freezing.
- ✓ **Latent heat of vaporization**: The amount of energy absorbed during vaporization and it is equivalent to the energy released during condensation.
- ✓ The magnitudes of the latent heats depend on the temperature or pressure at which the phase change occurs.
- ✓ At 1 atm pressure, the latent heat of fusion of water is 333.7 kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.
- ✓ The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation.

Variation of the standard atmospheric pressure and the boiling (saturation) temperature of water with altitude

Elevation, m	Atmospheric pressure, kPa	Boiling temperature, °C
0	101.33	100.0
1,000	89.55	96.5
2,000	79.50	93.3
5,000	54.05	83.3
10,000	26.50	66.3
20,000	5.53	34.7

Some Consequences of T_{sat} and P_{sat} Dependence

- ➢ A liquid cannot vaporize unless it absorbs energy in the amount of the latent heat of vaporization,
- ➢ The rate of vaporization of a fluid depends on the rate of heat transfer to it.
- ➢ The rate of heat transfer to the fluid and thus the rate of vaporization can be minimized by insulating the container heavily.
- ➢ During phase change, both T and P remain constant.
- ➢ A relatively simple empirical equation that correlates vapor pressure-temperature data extremely well is the **Antoine equation.**

$$\log_{10} p^* = A - \frac{B}{T + C}$$

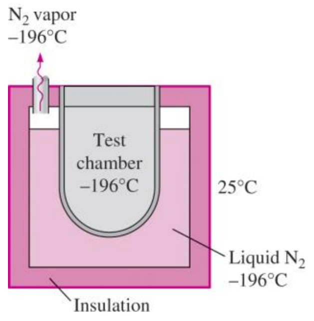
A, B and C are constants

Clausius–Clapeyron equation

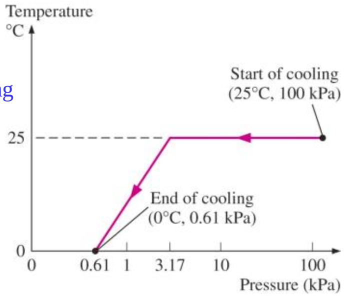
$$\ln p^* = -\frac{\Delta \hat{H}_v}{RT} + B$$

where B is a constant that varies from one substance to another.

Some Consequences of T_{sat} and P_{sat} Dependence



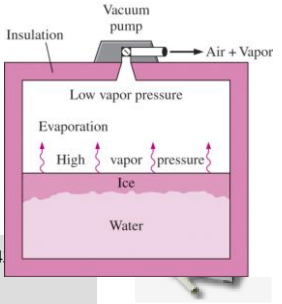
The variation of the temperature of fruits and vegetables with pressure during vacuum cooling from 25°C to 0°C (*reducing the pressure* of the sealed cooling chamber to the saturation pressure at the desired low temperature and evaporating water from the fluid to be cooled)



The temperature of liquid nitrogen exposed to the atmosphere remains constant at -196°C (T_b), and thus it maintains the test chamber at -196°C.

(cryogenic applications)

In 1775, ice was made by evacuating the air space in a water tank.



The State Principle

- Two independent, intensive, thermodynamic properties are required to fix the state of a **simple compressible system** (systems of commonly encountered pure substances, such as water or a uniform mixture of non-reacting gases in the absence of motion, gravity, and surface, magnetic, or electrical effects).

For example: P and v

T and u

x and h

Intensive thermodynamic properties:

h – specific enthalpy	**u – specific internal energy**	**x – quality (steam only)**	**s –specific entropy**
P –absolute pressure	**T – absolute temperature**	**v – specific volume**	**Less used:** **g - Gibbs free energy** **a - Helmholz free energy**

- The functional relations would be developed using experimental data and would depend explicitly on the particular chemical identity of the substances making up the system

Simple Compressible Substance

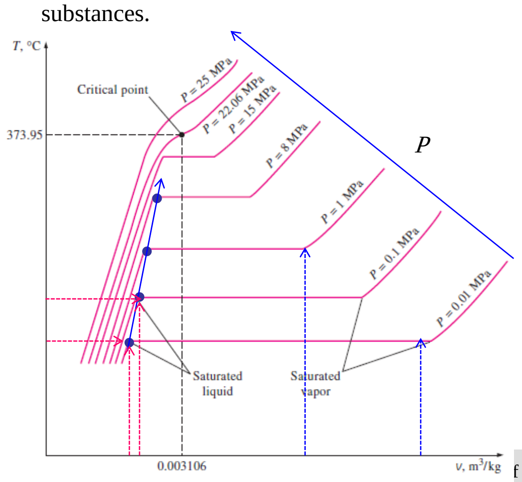
- A substance may be approximated as a simple compressible substance if effects due to other reversible work modes are negligible.
- Substances whose surface effects, magnetic effects, and electrical effects are insignificant when dealing with the substances. **But** changes in volume, such as those associated with-the-expansion of a gas in a cylinder, are very important.

  i.e. the only mode of energy transfer by work that can occur as a simple compressible system undergoes *quasiequilibrium* processes, is associated with volume change and is given by $\int p\, dV$.
- For example,
  - If the surface-to-volume ratio of a large body of water is small enough, then surface tension will not measurably affect the properties of the water except very near the surface.
  - On the other hand, surface tension will have a dramatic influence on the properties of a very small water droplet.

    i.e. a very small water droplet can't be treated accurately as a simple compressible substance, while a large body of water is approximated very well in this way.
- A simple compressible substance may exist in different phases: solid, liquid, or gas. Some substances have multiple solid phases, some even have multiple liquid phases (helium), but all have only one gas phase.

Property diagrams of Phase Change Processes

- The variations of properties during phase-change processes are best studied and understood with the help of property diagrams such as the T-v, P-v, and P-T diagrams for pure substances.



T-V diagrams

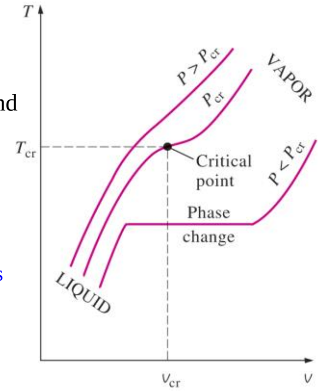
By increasing the pressure,

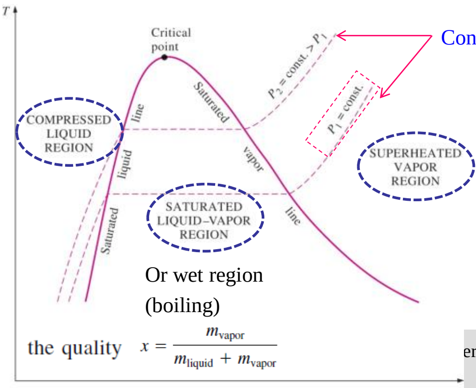
- Water starts boiling at a much higher T
- The specific volume of the saturated liquid is larger and the specific volume of the saturated vapor is smaller than the corresponding values at 1 atm pressure
- As the pressure is increased further, this saturation line continues to shrink, and it becomes a point when the pressure reaches 22.06 MPa for the case of water.
- This point is called the **critical point,** and it is defined as *the point at which the saturated liquid and saturated vapor states are identical*

T-V diagrams

At pressures above the critical pressure,

- There is not a distinct phase change process
- The specific volume of the substance continually increases, and at all times there is only one phase present
- Above the critical state, there is no line that separates the compressed liquid region and the superheated vapor region.

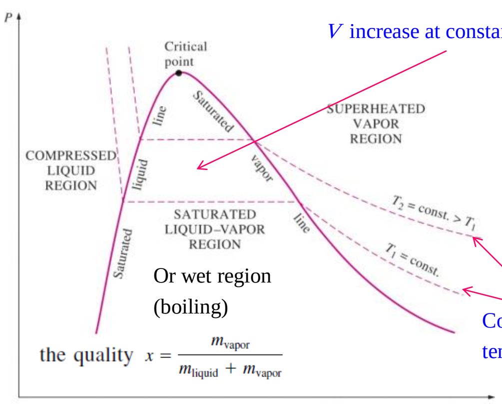




the quality $x = \frac{m_{vapor}}{m_{liquid} + m_{vapor}}$

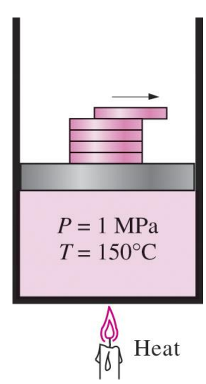
- The saturated liquid states can be connected by a line called the **saturated liquid line,** and saturated vapor states in the same figure can be connected by another line, called the **saturated vapor line**

P-V diagrams



the quality $x = \frac{m_{vapor}}{m_{liquid} + m_{vapor}}$

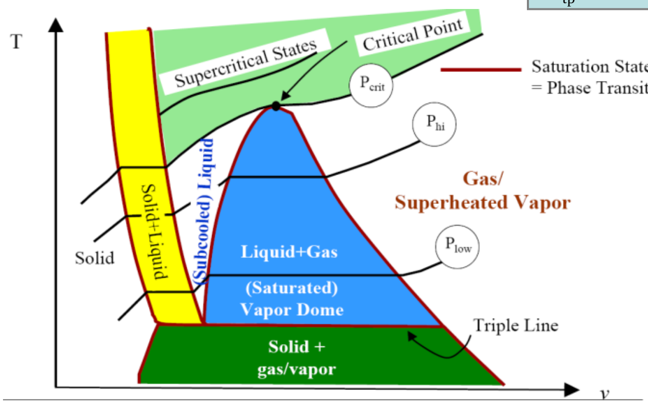
P-v diagram of a pure substance.

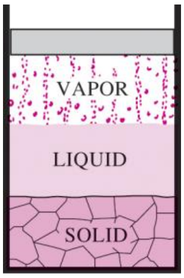


The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

Extending the Diagrams to Include the Solid Phase

For water,
T_{tp} = 0.01°C
P_{tp} = 0.6117 kPa





At triple-point pressure and temperature, a substance exists in three phases in equilibrium.

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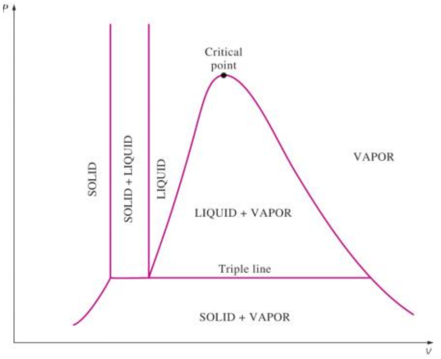
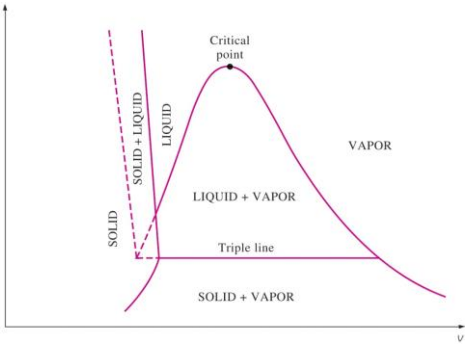
Extending the Diagrams to Include the Solid Phase



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



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

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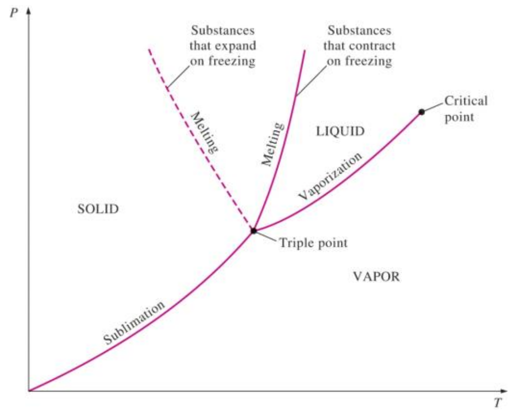
P-T diagrams

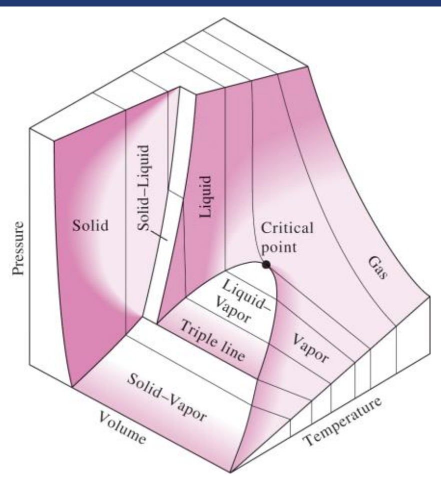
Sublimation: Passing from the solid phase directly into the vapor phase.

At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).

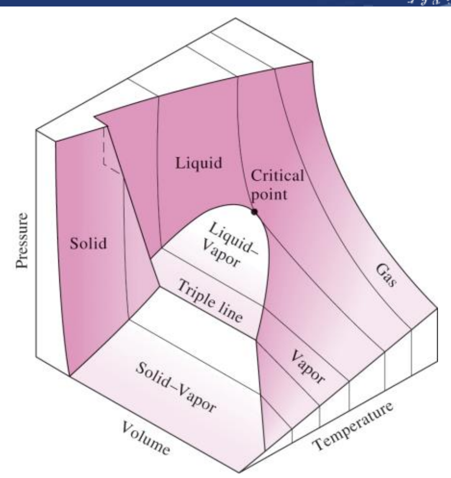


P-T diagram of pure substances.

The P-v-T Surface



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



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

Property Tabls

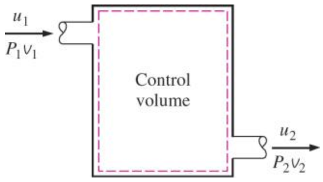
- For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations.
- Therefore, properties are frequently presented in the form of tables.
- Some thermodynamic properties can be measured easily, but others cannot and are calculated by using the relations between them and measurable properties.
- The results of these measurements and calculations are presented in tables in a convenient format.
- A separate table is prepared for each region of interest such as the superheated vapor, compressed liquid, and saturated (mixture regions).

Enthalpy—A Combination Property

$h = u + Pv$ (kJ/kg)

$H = U + PV$ (kJ)

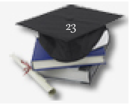
$u = h - Pv.$



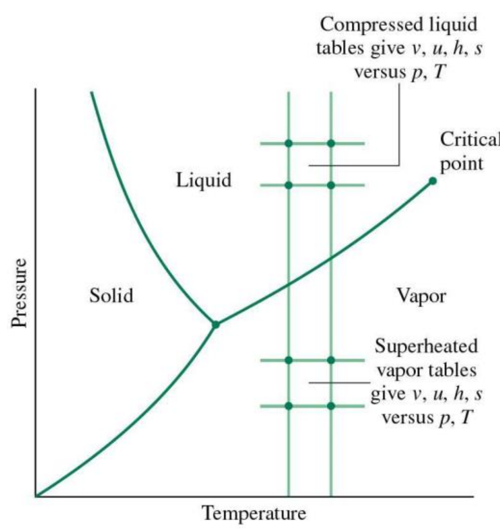
The combination $u + P*v$ is frequently encountered in the analysis of control volumes.

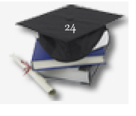
$\text{kPa} \cdot \text{m}^3 \equiv \text{kJ}$
$\text{kPa} \cdot \text{m}^3/\text{kg} \equiv \text{kJ/kg}$
$\text{bar} \cdot \text{m}^3 \equiv 100 \text{ kJ}$
$\text{MPa} \cdot \text{m}^3 \equiv 1000 \text{ kJ}$
$\text{psi} \cdot \text{ft}^3 \equiv 0.18505 \text{ Btu}$

The product *pressure* × *volume* has energy units.



Property Tables





Saturated Liquid and Saturated Vapor States

- **Table A–4**: Saturation properties of water under temperature.
- **Table A–5**: Saturation properties of water under pressure.

v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor

v_{fg} = difference between v_g and v_f (that is, $v_{fg} = v_g - v_f$)

Enthalpy of vaporization, h_{fg} **(Latent heat of vaporization):** The amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure.

A partial list of Table A–4.

Temp. °C T	Sat. press. kPa P_{sat}	Specific volume m^3/kg: Sat. liquid v_f	Specific volume m^3/kg: Sat. vapor v_g
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

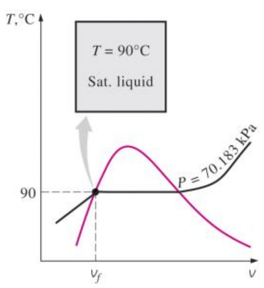
Specific temperature

Corresponding saturation pressure

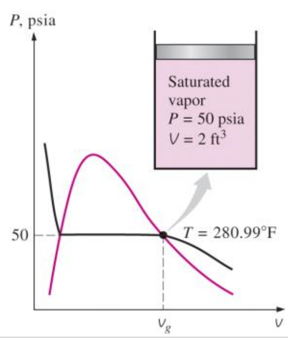
Specific volume of saturated liquid

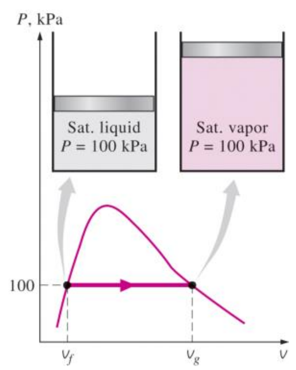
Specific volume of saturated vapor

Saturated Liquid and Saturated Vapor States



Examples: Saturated liquid and saturated vapor states of water on T-v and P-v diagrams.





Saturated Liquid–Vapor Mixture

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**.

The properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapor.

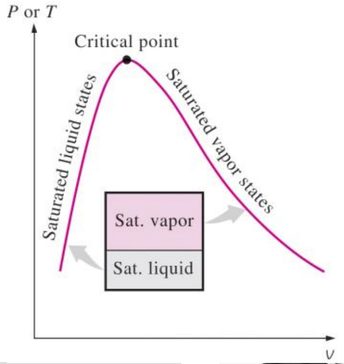
Temperature and pressure are dependent properties for a mixture.

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}}$$

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

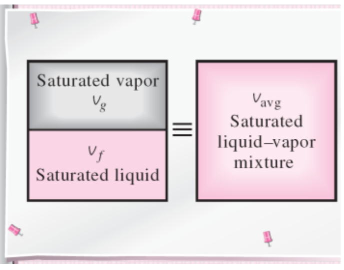
The relative amounts of liquid and vapor phases in a saturated mixture are specified by the ***quality x***.

(1-x) gives **Moisture Content**



Saturated Liquid–Vapor Mixture

- *A two-phase system can be treated as a homogeneous mixture for convenience.*
- *For a tank* contains a saturated liquid–vapor mixture



$$V = V_f + V_g$$

$$V = mv \longrightarrow m_t v_{\text{avg}} = m_f v_f + m_g v_g$$

$$m_f = m_t - m_g \longrightarrow m_t v_{\text{avg}} = (m_t - m_g)v_f + m_g v_g$$

Dividing by m_t $\qquad v_{\text{avg}} = (1 - x)v_f + xv_g \qquad$ since $x = m_g/m_t$.

$$v_{\text{avg}} = v_f + xv_{fg} \qquad (\text{m}^3/\text{kg})$$

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

$$\Rightarrow \quad x = \frac{v_{\text{avg}} - v_f}{v_{fg}}$$

Saturated Liquid–Vapor Mixture

$y \rightarrow v, u,$ or $h.$

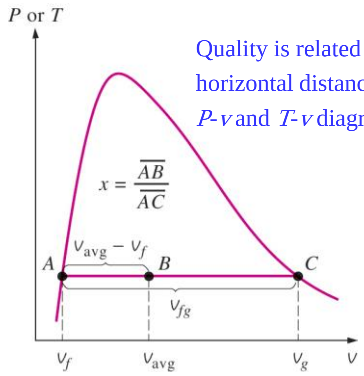
$y_{avg} = y_f + xy_{fg}$

$y_f \leq y_{avg} \leq y_g$

$\Rightarrow$

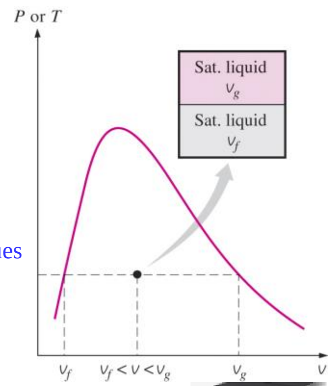
$u_{avg} = u_f + xu_{fg}$ (kJ/kg)

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



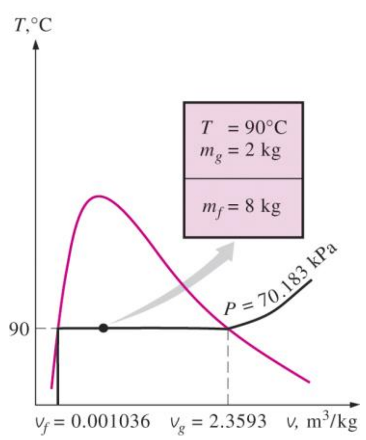
Quality is related to the horizontal distances on *P-v* and *T-v* diagrams.

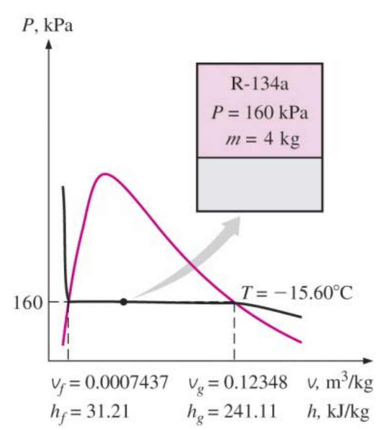
The *v* value of a saturated liquid–vapor mixture lies between the v_f and v_g values at the specified *T* or *P*.



Saturated Liquid–Vapor Mixture

Examples: Saturated liquid-vapor mixture states on *T-v* and *P-v* diagrams.





Quality Relations

LET b = ANY INTENSIVE PROPERTY

– (b = v, u, h, s, etc.)

$$x = \frac{b - b_f}{b_g - b_f} = \frac{b - b_f}{b_{fg}}$$

$$b = b_f + x \cdot b_{fg}$$

$$b_{fg} = b_g - b_f$$

$$b = x \cdot b_g + (1 - x) \cdot b_f$$

Superheated Vapor

- In the region to the right of the saturated vapor line and at temperatures above the critical point temperature, a substance exists as superheated vapor.
- In this region, temperature and pressure are independent properties.

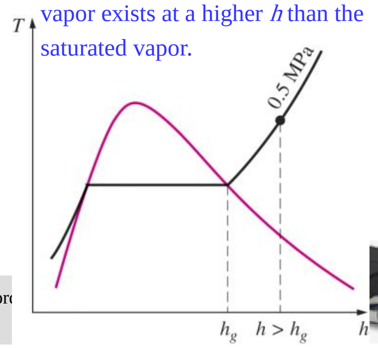
T,°C	v m³/kg	u kJ/kg	h kJ/kg
	P = 0.1 MPa (99.61°C)		
Sat.	1.6941	2505.6	2675.0
100	1.6959	2506.2	2675.8
150	1.9367	2582.9	2776.6
⋮	⋮	⋮	⋮
1300	7.2605	4687.2	5413.3
	P = 0.5 MPa (151.83°C)		
Sat.	0.37483	2560.7	2748.1
200	0.42503	2643.3	2855.8
250	0.47443	2723.8	2961.0

A partial listing of Table A–6.

Compared to saturated vapor, superheated vapor is 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)

At a specified P, superheated vapor exists at a higher h than the saturated vapor.



Compressed Liquid

- The compressed liquid properties depend on temperature much more strongly than they do on pressure.

  $y \cong y_{f @ T}$ $y \rightarrow v$, u, or h

- A more accurate relation for h

$$h \cong h_{f @ T} + v_{f @ T}(P - P_{sat @ T})$$

Given: P and T

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

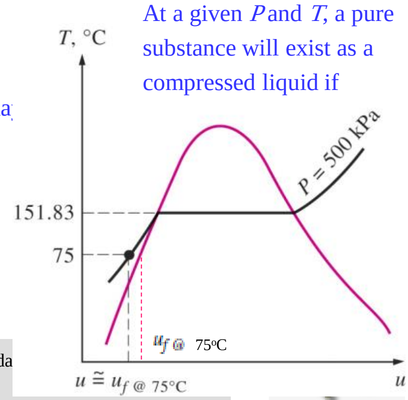
Compressed liquid is characterized by

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)

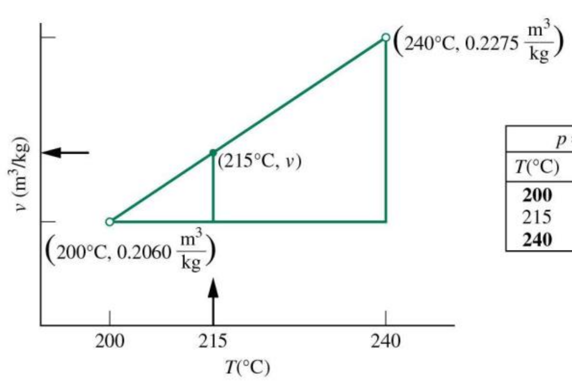
A compressed liquid may be approximated as a saturated liquid at the given temperature.

At a given P and T, a pure substance will exist as a compressed liquid if

$$T < T_{sat @ P}$$



Linear Interpolation: Between values in the tables



p = 10 bar	
T(°C)	v (m³/kg)
200	**0.2060**
215	v = ?
240	**0.2275**

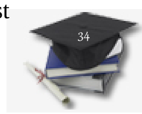
$$\frac{T_L - T}{T_H - T_L} = \frac{v_L - v}{v_H - v_L}$$

Subscripts:

L – Value in table at lower end

H – Value in table at upper end

None – value of interest



Reference State and Reference Values

- The values of *u*, *h*, and *s* cannot be measured directly, and they are calculated from measurable properties using the relations between properties.
- However, those relations give the *changes* in properties, not the values of properties at specified states.
- Therefore, we need to choose a convenient *reference state* and assign a value of *zero* for a convenient property or properties at that state.
- The reference state for water is 0.01°C and for R-134a is -40°C in tables.
- Some properties may have negative values as a result of the reference state chosen.
- Sometimes different tables list different values for some properties at the same state as a result of using a different reference state.
- However, In thermodynamics we are concerned with the *changes* in properties, and the reference state chosen is of no consequence in calculations.

Saturated water—Temperature table

		Specific volume, m^3/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	0.6117	0.001000	206.00	0.000	2374.9	2374.9	0.001	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.019	2360.8	2381.8	21.020	2489.1	2510.1	0.0763	8.9487	9.0249

Saturated refrigerant-134a—Temperature table

		Specific volume, m^3/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
−40	51.25	0.0007054	0.36081	−0.036	207.40	207.37	0.000	225.86	225.86	0.00000	0.96866	0.96866

The Ideal Gas Equation of State

- **Equation of state**: Any equation that relates the pressure, temperature, and specific volume of a substance.
- The simplest and best-known equation of state for substances in the gas phase is the ideal-gas equation of state. This equation predicts the *P-v-T* behavior of a gas quite accurately within some properly selected region.

$$P = R\left(\frac{T}{v}\right) \qquad Pv = RT$$

Ideal gas equation of state

$$R = \frac{R_u}{M} \qquad (\text{kJ/kg} \cdot \text{K or kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})$$

R: gas constant

M: molar mass (kg/kmol)

R_u: universal gas constant

$$R_u = \begin{cases} 8.31447 \text{ kJ/kmol} \cdot \text{K} \\ 8.31447 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\ 0.0831447 \text{ bar} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\ 1.98588 \text{ Btu/lbmol} \cdot \text{R} \\ 10.7316 \text{ psia} \cdot \text{ft}^3/\text{lbmol} \cdot \text{R} \\ 1545.37 \text{ ft} \cdot \text{lbf/lbmol} \cdot \text{R} \end{cases}$$

Substance	*R*, kJ/kg·K
Air	0.2870
Helium	2.0769
Argon	0.2081
Nitrogen	0.2968

Different substances have different gas constants.

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The Ideal Gas Equation of State

Mass = Molar mass × Mole number

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

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

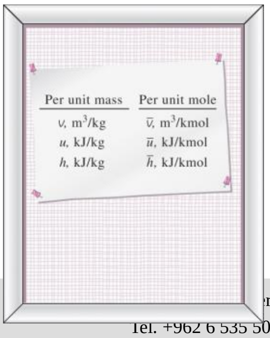
Ideal gas equation at two states for a fixed mass

$$V = m v \longrightarrow PV = mRT$$

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

$$V = N\bar{v} \longrightarrow P\bar{v} = R_u T$$

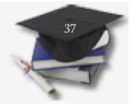
Various expressions of ideal gas equation



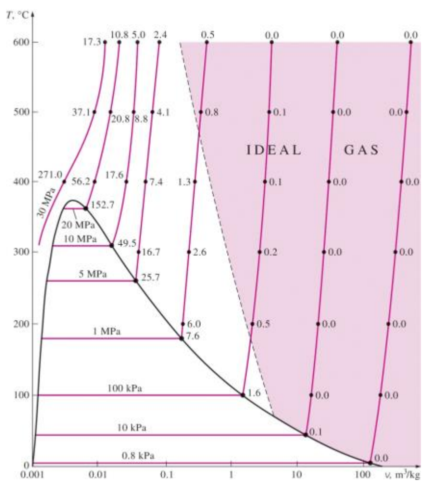
Per unit mass	Per unit mole
v, m³/kg	$\bar{v}$, m³/kmol
u, kJ/kg	$\bar{u}$, kJ/kmol
h, kJ/kg	$\bar{h}$, kJ/kmol

Properties per unit mole are denoted with a bar on the top.

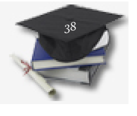
- The ideal-gas relation often is not applicable to real gases; thus, care should be exercised when using it.
- **Real gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).**



Is Water Vapor an Ideal Gas?



- At pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent).
- At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line.
- In air-conditioning applications, the water vapor in the air can be treated as an ideal gas. Why?
- In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.
- 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.

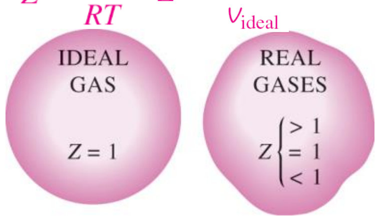


Compressibility Factor Z

- **Compressibility factor *Z*:** A factor that accounts for the deviation of real gases from ideal-gas behavior at a given temperature and pressure.

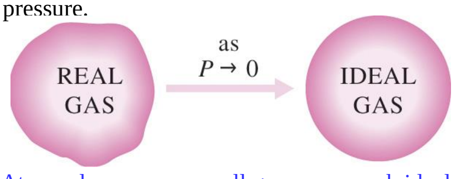
$$Pv = ZRT$$

$$Z = \frac{Pv}{RT} \qquad Z = \frac{v_{actual}}{v_{ideal}}$$



The compressibility factor is unity for ideal gases.

- The farther away *Z* is from unity, the more the gas deviates from ideal-gas behavior.
- *Gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).*
- **Question**: What is the criteria for low pressure and high temperature?
- **Answer**: The pressure or temperature of a gas is high or low relative to its critical temperature or pressure.

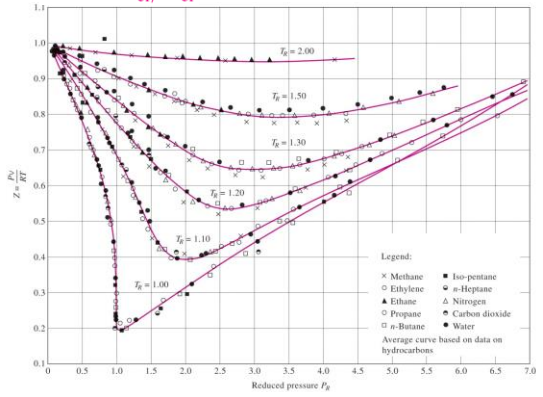


At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).

Compressibility Factor Z

$$P_R = \frac{P}{P_{cr}} \qquad T_R = \frac{T}{T_{cr}}$$

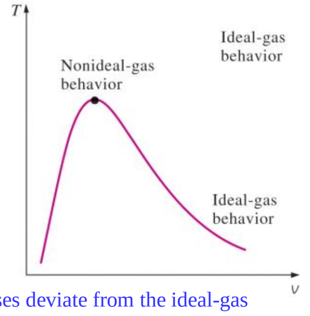
$$v_R = \frac{v_{actual}}{RT_{cr}/P_{cr}}$$ Pseudo-reduced specific volume



Comparison of *Z* factors for various gases.

$$\left.\begin{aligned} P_R &= \frac{P}{P_{cr}} \\ v_R &= \frac{v}{RT_{cr}/P_{cr}} \end{aligned}\right\} Z = \ldots \text{ (Fig. A–15)}$$

Z can also be determined from a knowledge of P_R and v_R.



Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

Other Equation of States

- Several equations have been proposed to represent the P-v-T behavior of substances accurately over a larger region with no limitations.

Van der Waals Equation of State

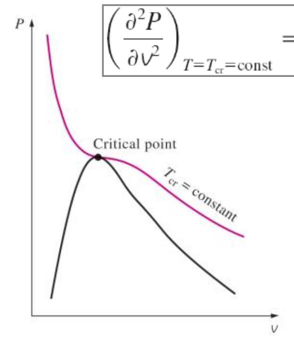
$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

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

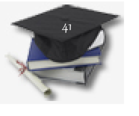
- This model includes two effects not considered in the ideal-gas model: the *intermolecular attraction forces* and the *volume occupied by the molecules themselves*. The accuracy of the van der Waals equation of state is often inadequate.

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

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



Critical isotherm of a pure substance has an inflection point at the critical state.



Other Equation of States

Beattie-Bridgeman Equation of State

$$P = \frac{R_uT}{\bar{v}^2}\left(1 - \frac{c}{\bar{v}T^3}\right)(\bar{v} + B) - \frac{A}{\bar{v}^2}$$

$$A = A_0\left(1 - \frac{a}{\bar{v}}\right) \qquad B = B_0\left(1 - \frac{b}{\bar{v}}\right)$$

The constants are given in Table 3–4 for various substances. It is known to be reasonably accurate for densities up to about $0.8\rho_{cr}$.

Benedict-Webb-Rubin Equation of State

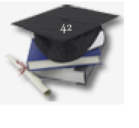
$$P = \frac{R_uT}{\bar{v}} + \left(B_0R_uT - A_0 - \frac{C_0}{T^2}\right)\frac{1}{\bar{v}^2} + \frac{bR_uT - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3T^2}\left(1 + \frac{\gamma}{\bar{v}^2}\right)e^{-\gamma/\bar{v}^2}$$

The constants are given in Table 3–4. This equation can handle substances at densities up to about 2.5 ρ_{cr}.

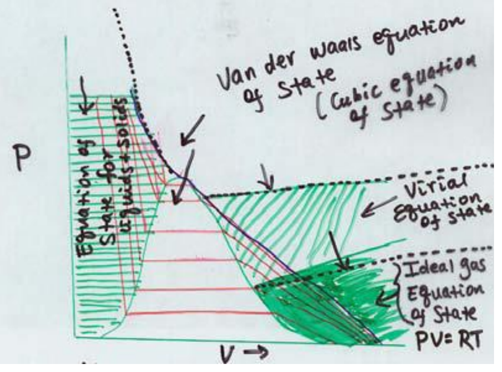
Virial Equation of State

$$P = \frac{RT}{v} + \frac{a(T)}{v^2} + \frac{b(T)}{v^3} + \frac{c(T)}{v^4} + \frac{d(T)}{v^5} + \ldots$$

The coefficients $a(T)$, $b(T)$, $c(T)$, and so on, that are functions of temperature alone are called *virial coefficients*.



Equation of States



(1) At low Pressure, Ideal gas EoS for gases

$$\frac{P\hat{V}}{RT} = 1$$

(2) At moderate pressure, virial equation of State (in the gas region)

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}}$$

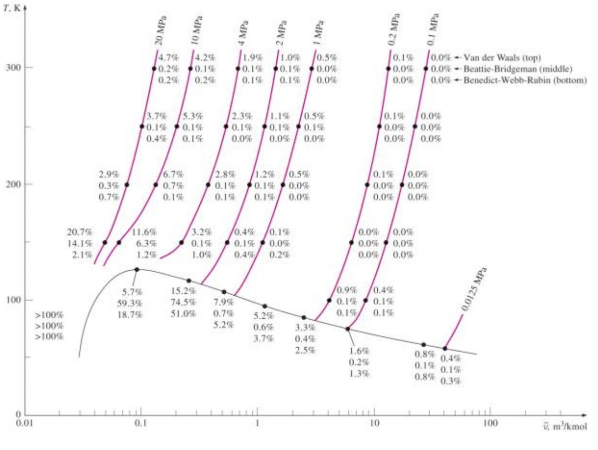
(3) Van der Waals (Cubic) EoS for the two phase region and fluid region

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

(4) Liquid EoS for incompressibles??

$$Pv = ZRT$$

Other Equation of States



van der Waals: 2 constants. Accurate over a limited range.

Beattie-Bridgeman: 5 constants. Accurate for $\rho \leq 0.8\rho_{cr.}$

Benedict-Webb-Rubin: 8 constants. Accurate for $\rho \leq 2.5\rho_{cr.}$

Strobridge: 16 constants. More suitable for computer calculations.

Virial: may vary. Accuracy depends on the number of terms used.

Complex equations of state represent the *P-v-T* behavior of gases more accurately over a wider range.

Percentage of error involved in various equations of state for nitrogen

(% error = $[(|v_{table} - v_{equation}|)/v_{table}] \times 100$).

Compressibility & Volume Expansion Coefficients

- How does fluid volume change with P and T?
  - ✓ Fluids expand as $T\uparrow$ or $P\downarrow$
  - ✓ Fluids contract as $T\downarrow$ or $P\uparrow$
- Need fluid properties that relate volume changes to changes in P and T.

$$v = v(T, P)$$

$$dv = \underbrace{\left(\frac{\partial v}{\partial T}\right)_P}_{v\beta} dT + \underbrace{\left(\frac{\partial v}{\partial P}\right)_T}_{-\frac{v}{\kappa}} dP$$

The variation of the density of a fluid with temperature at constant pressure.

- Coefficient of volume expansion

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P$$

- Coefficient of compressibility **(Bulk Modulus)**

$$\kappa = -v\left(\frac{\partial P}{\partial v}\right)_T = \rho\left(\frac{\partial P}{\partial \rho}\right)_T$$

The isothermal compressibility $\alpha = \frac{1}{\kappa} = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$ (1/Pa)

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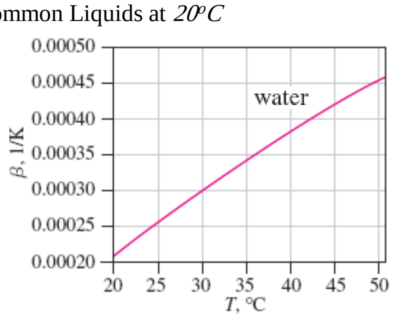
Compressibility & Volume Expansion Coefficients

$$\beta \approx \frac{\Delta v/v}{\Delta T} = -\frac{\Delta\rho/\rho}{\Delta T} \quad \text{(at constant } P\text{)} \qquad \kappa \cong -\frac{\Delta P}{\Delta v/v} \cong \frac{\Delta P}{\Delta\rho/\rho} \quad (T = \text{constant})$$

Coefficient of compressibility Values κ for Several Common Liquids at 20^oC

Liquid	κ (GPa)
Gasoline	0.958
Mercury	25.5
Methanol	0.83
SAE 30W oil	1.38
Water	2.19
Seawater (30% salinity)	2.33



$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP = (\beta\, dT - \alpha\, dP)v \qquad \frac{\Delta v}{v} = -\frac{\Delta \rho}{\rho} \cong \beta\,\Delta T - \alpha\,\Delta P$$

- A large value of k indicates that a large change in pressure is needed to cause a small fractional change in volume, and thus a fluid with a large k is essentially incompressible.
- A large value of β for a fluid means a large change in density with temperature.

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Lecture 5 Part 2

Please, go to lecture 5 part 2 to continue with the equation of states. This part is already discussed in the principle 1 course (Lec 9_Single-Phase Systems) and in **Elementary Principles of Chemical Processes,** Third Edition, Richard M. Felder and Ronald W. Rousseau John Wiley and Sons, Inc., 1999)

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Examples

A piston–cylinder device contains 2 ft^3 of saturated water vapor at 50-psia pressure. Determine the temperature and the mass of the vapor inside the cylinder

A mass of 200 g of saturated liquid water is completely vaporized at a constant pressure of 100 kPa. Determine (*a*) the volume change and (*b*) the amount of energy transferred to the water.

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Examples

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.

Example Cont.

Examples

An 80-L vessel contains 4 kg of refrigerant-134a at a pressure of 160 kPa. Determine (*a*) the temperature, (*b*) the quality, (*c*) the enthalpy of the refrigerant, and (*d*) the volume occupied by the vapor phase.

Example Cont.

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Example

Determine the missing properties and the phase descriptions in the following table for water:

	T, °C	P, kPa	u, kJ/kg	x	Phase description
(a)		200		0.6	
(b)	125		1600		
(c)		1000	2950		
(d)	75	500			
(e)		850		0.0	

Example Cont.

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