# *Properties of Pure Substances*

| **Reading** | **Problems** |
|---|---|
| 4-1 → 4-7 | 4-41, 4-54, 4-58, 4-79, 4-95 |
| 5-3 → 5-5 | |

## Pure Substances

- it has a fixed chemical composition throughout (chemically uniform)
- a homogeneous mixture of various chemical elements or compounds can also be considered as a pure substance (uniform chemical composition)

## Phases of Pure Substances

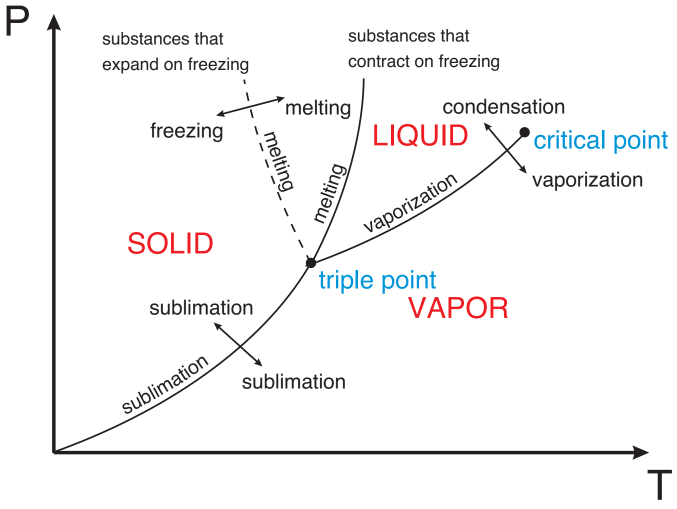
**Solids:** strong molecular bonds

**Liquids:** molecules are no longer in a fixed position relative to one another

**Gases:** there is no molecular order

## Behavior of Pure Substances (Phase Change Processes)

- all pure substances exhibit the same general behavior.
  - one exception is that most contract on freezing. $H_2O$ (and a few more) expand on freezing.
- phase change processes:
- **Critical point:** is the point at which the liquid and vapor phases are not distinguishable (we will talk about this more)
- **Triple point:** is the point at which the liquid, solid, and vapor phases can exist together



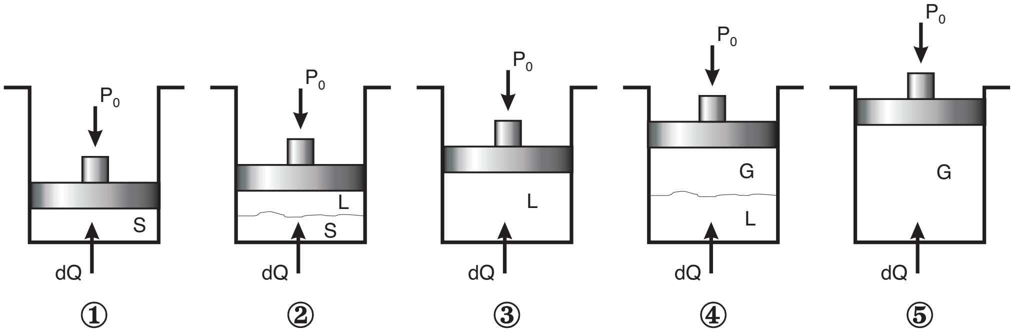
**Phase Diagram**

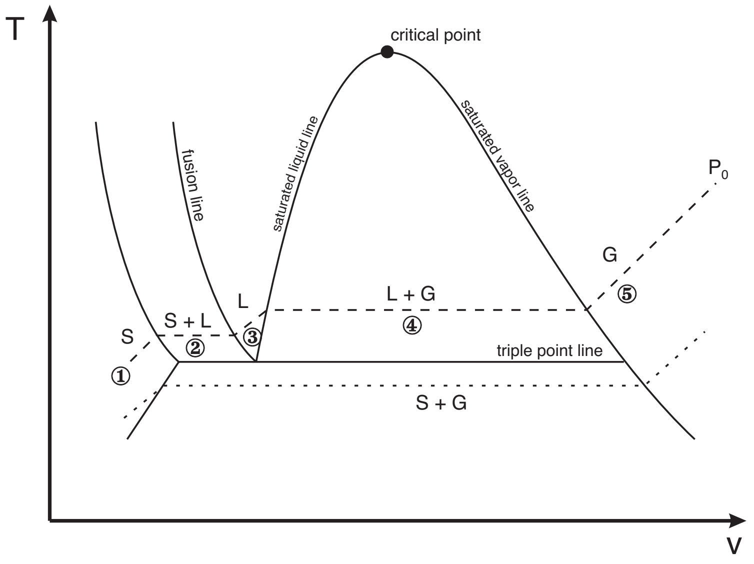
|  | **Critical Point**[1] |  | **Triple Point**[2] |  |
|---|---|---|---|---|
|  | $P\ (MPa)$ | $T\ (°C)$ | $P\ (MPa)$ | $T\ (°C)$ |
| $H_2O$ | 22.06 | 373.95 | 0.00061 | 0.01 |
| $O_2$ | 5.08 | $-118.35$ | 0.000152 | $-218.79$ |
| $CO_2$ | 7.39 | 31.05 | 0.517 | 56.6 |
| $N$ | 3.39 | $-146.95$ | 0.0126 | $-209.97$ |
| $He$ | 0.23 | $-267.85$ | 0.0051 | $-270.96$ |

**1** - see Table A-1 for other substances **2** - see Table 4.3 for other substances

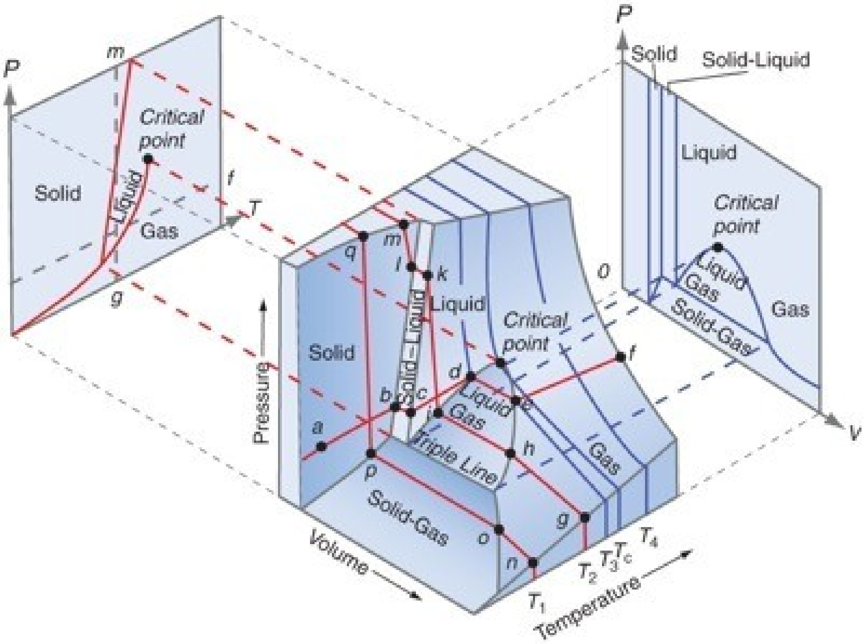
## $T - v$ *Diagram for a Simple Compressible Substance*

consider an experiment in which a substance starts as a solid and is heated up at constant pressure until it all becomes as gas





## *The P-v-T Surface Diagram*



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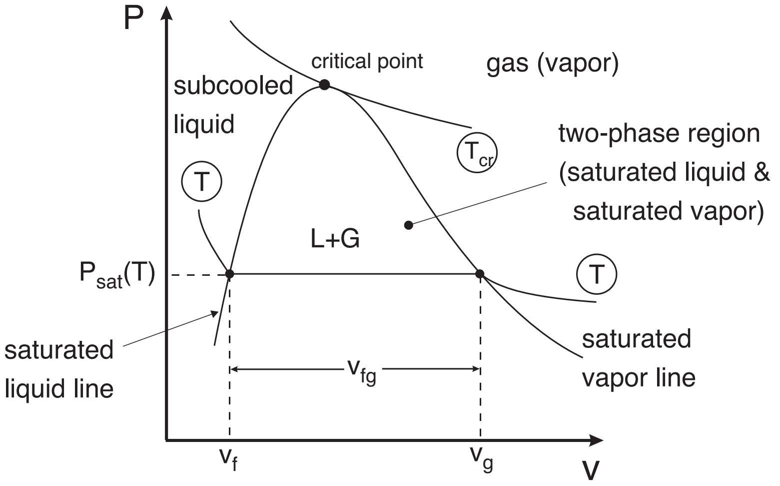
- if P-v-T is projected onto a pressure-temperature plane we obtain a phase diagram
- if we project onto a pressure-volume plane we obtain the familiar P-v diagram for a substance (likewise for T-v)

## *The Vapor Dome (Two Phase Region)*



**specific volume:**
$v_f$, $v_g$ and $v_{fg} = v_g - v_f$

**internal energy:**
$u_f$, $u_g$ and $u_{fg} = u_g - u_f$

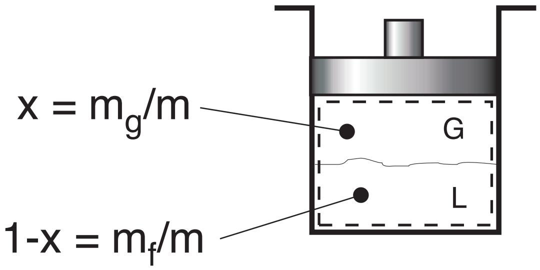
**specific enthalpy:**
$h_f$, $h_g$ and $h_{fg} = h_g - h_f$

**specific entropy:**
$s_f$, $s_g$ and $s_{fg} = s_g - s_f$

- the subscripts denote: $f$ - saturated liquid (fluid) and $g$ - saturated vapor (gas)
- given the shape of the vapor dome, as $T \uparrow$ or $P \uparrow \quad \Rightarrow \quad h_{fg} \downarrow$

## *Quality*

We need to define a new thermodynamic property: **Quality** $\equiv x = \dfrac{m_g}{m} = \dfrac{m_g}{m_g + m_f}$



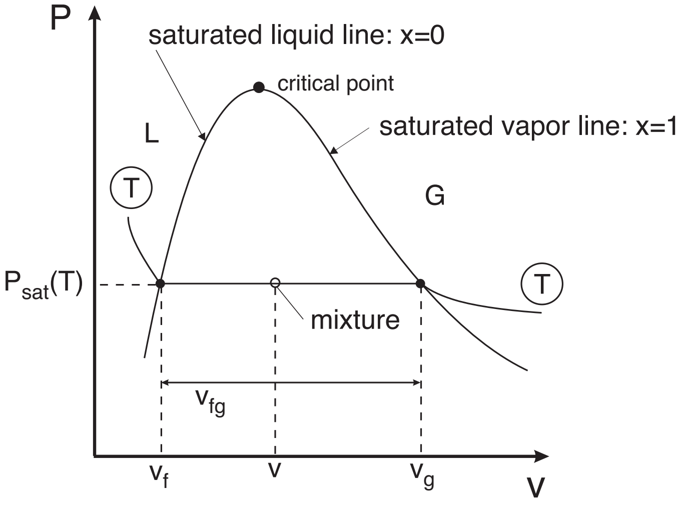
total mass of mixture $\Rightarrow$ $m = m_g + m_f$

mass fraction of the gas $\Rightarrow$ $x = m_g/m$

mass fraction of the liquid $\Rightarrow$ $1 - x = m_f/m$

## *Properties of Saturated Mixtures*

- To fix the state we require $(T, x), (T, v), (P, x) \ldots$
- all the calculations done in the vapor dome can be performed using Tables.
  - in Table A-4, the properties are listed under Temperature
  - in Table A-5, the properties are listed under Pressure
- other properties are calculated as mass-average values of the saturated quantities

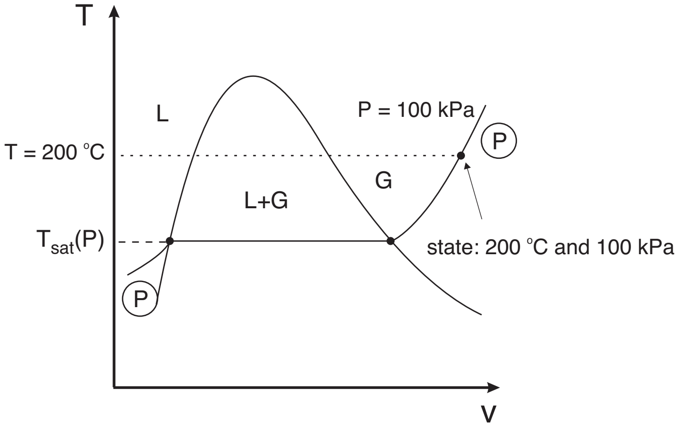


$$
\begin{aligned}
v &= \frac{V}{m} = \frac{V_f + V_g}{m} = \frac{m_f v_f + m_g v_g}{m} = (1 - x)\, v_f + x\, v_g \\
&= v_f + x(v_g - v_f) = v_f + x\, v_{fg} \\
x &= \frac{v - v_f}{v_{fg}}
\end{aligned}
$$

$$
\begin{aligned}
u &= (1 - x) u_f + x\, u_g = u_f + x\, u_{fg} \Rightarrow x = \frac{u - u_f}{u_{fg}} \\
h &= (1 - x) h_f + x\, h_g = h_f + x\, h_{fg} \Rightarrow x = \frac{h - h_f}{h_{fg}} \\
s &= (1 - x) s_f + x\, s_g = s_f + x\, s_{fg} \Rightarrow x = \frac{s - s_f}{s_{fg}}
\end{aligned}
$$

## *Properties of Superheated Vapor*

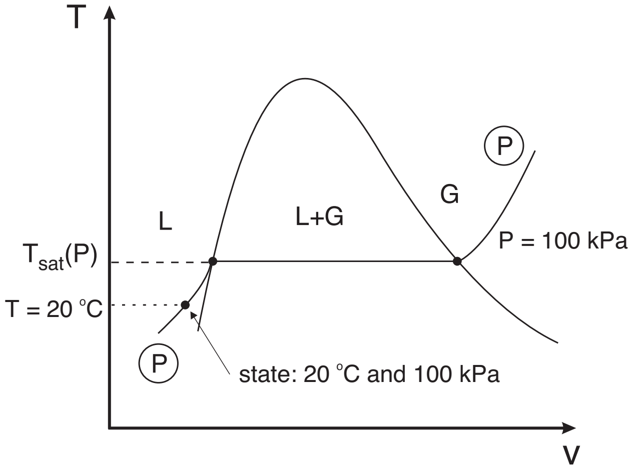
- superheated means $T > T_{sat}$ at the prevailing $P$, eg. water at $100\ kPa$ has a saturation temperature of $T_{sat}(P) = 99.63\ °C$.
- To fix the state we require $(T, v), (P, T) \ldots$



- superheated vapor is a single phase
  - $T$ and $P$ are independent of each other in the single-phase region
  - properties are typically calculated as a function of $T$ and $P$
- if $T >> T_{cr}$ or $P << P_{cr}$ then ideal gas behavior applies and the ideal gas equations of state can be used
- Table A-6 for superheated water

## *Properties of Sub-cooled (Compressed) Liquid*

- sub-cooled liquid means $T < T_{sat}$ at the prevailing $P$, eg. water at $20\ °C$ and $100\ kPa$ has a saturation temperature of $T_{sat}(P) = 99.63\ °C$.



- can be treated as incompressible (independent of $P$)

$$\begin{aligned} v &= v(T,P) \Rightarrow v \approx v(T) = v_f(T) \\ u &= u(T,P) \Rightarrow u \approx u(T) = u_f(T) \\ s &= s(T,P) \Rightarrow s \approx s(T) = s_f(T) \end{aligned}$$

- for enthalpy:

$$\begin{aligned} h(T,P) &= u(T,P) + v(T,P)P \approx u_f(T) + v_f(T)P \\ &= \underbrace{u_f(T) + v_f(T)P_{sat}(T)}_{h_f(T)} + v_f(T)[P - P_{sat}(T)] \\ &= h_f(T) + v_f(T)[P - P_{sat}(T)] \end{aligned}$$

**Example 2-1:** A saturated mixture of R-134a with a liquid volume fraction of $10\%$ and a pressure of $200\ kPa$ fills a rigid container whose volume is $0.5\ m^3$. Find the quality of the saturated mixture and the total mass of the R134-a.

## Equations of State: Calculate the Properties of Gaseous Pure Substances

**Tables:** water (Tables A-4 → A-8, A-15), R134a (Tables A-11 → A-13, A-16)

**Graphs:** water (Figures A-9 & A-10), R134a (Figure A-14)

**Equations:** (Table A-2c), (Table 4-4)

- *a better alternative for gases:* use the Equation of State which is a functional relationship between $P, v,$ and $T$ (3 measurable properties)

### Ideal Gases

- gases that adhere to a pressure, temperature, volume relationship

$$Pv = RT \qquad \text{or} \qquad PV = mRT$$

are referred to as ideal gases

  - where $R$ is the gas constant for the specified gas of interest ($R = R_u/\tilde{M}$)

$$R_u = \text{Universal gas constant, } \equiv 8.314\ kJ/(kmol \cdot K)$$

$$\tilde{M} = \text{molecular wieght (or molar mass) of the gas (see Table A-1))}$$

### Real Gases

- experience shows that **real gases** obey the following equation closely:

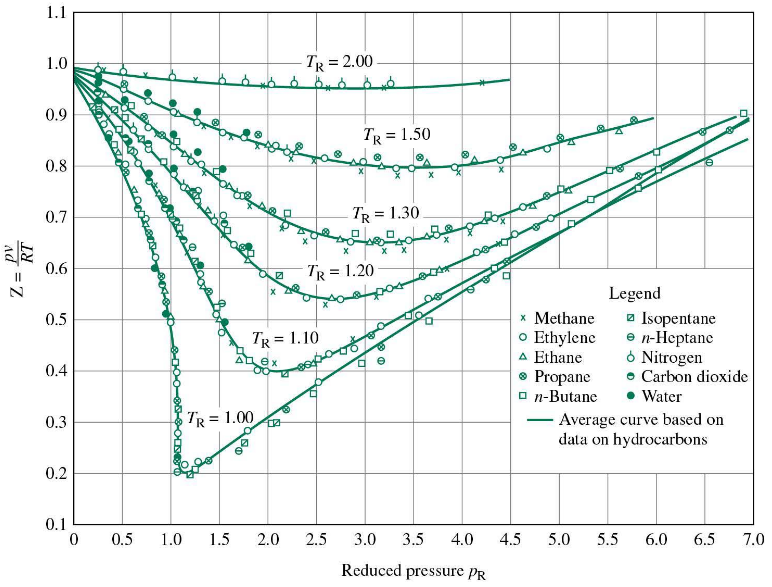
$$Pv = ZRT \quad (T \text{ and } P \text{ are in absolute terms})$$

where $Z$ is the compressibility factor

- if we "reduce" the properties with respect to the values at the critical point, i.e.

$$\text{reduced pressure} = P_r = \frac{P}{P_c} \qquad P_c = \text{critical pressure}$$

$$\text{reduced temperature} = T_r = \frac{T}{T_c} \qquad T_c = \text{critical temperature}$$



## *Reference Values for $u$, $h$, $s$*

- values of enthalpy, $h$ and entropy, $s$ listed in the tables are with respect to a datum where we arbitrarily assign the zero value. For instance:

  **Table A-4, A-5:** saturated liquid - the reference for both $h_f$ and $s_f$ is taken at the triple point and $T_{ref} = 0.01\ ^\circ C$. This is shown as follows:

$$u_f(@T = 0.01\ ^\circ C) = 0\ kJ/kg$$

$$h_f(@T = 0.01\ ^\circ C) = 0\ kJ/kg$$

$$s_f(@T = 0.01\ ^\circ C) = 0\ kJ/kg \cdot K$$

  **Table A-11, A-12, & A-13:** saturated R134a - the reference for both $h_f$ and $s_f$ is taken as $-40\ ^\circ C$. This is shown as follows:

$$h_f(@T = -40\ ^\circ C) = 0\ kJ/kg$$

$$h_f(@T = -40\ ^\circ C) = 0\ kJ/kg$$

$$s_f(@T = -40\ ^\circ C) = 0\ kJ/kg \cdot K$$

  **Others:** sometimes tables will use $0\ K$ as the reference for all tables. While this standardizes the reference, it tends to lead to larger values of enthalpy and entropy.

- for the most part the choice of a reference temperature in the property tables does not affect us because we generally deal with $\Delta h$, $\Delta u$, or $\Delta s$. The calculated difference of properties will be identical regardless of the reference temperature. Note: Be careful not to use values from different tables in the same calculation in the event that a difference reference temperature is used in the tables.

# Calculation of the Stored Energy

- how do we calculate $\Delta U$ and $\Delta H$?

  1. one can often find $u_1$ and $u_2$ in the thermodynamic tables (like those examined for the states of water).
  2. we can also explicitly relate $\Delta U$ and $\Delta H$ to $\Delta T$ (as mathematical expressions) by using the thermodynamic properties $C_p$ and $C_v$.

- the calculation of $\Delta u$ and $\Delta h$ for an ideal gas is given as

$$\Delta u = u_2 - u_1 \;=\; \int_1^2 C_v(T)\,dT \quad (kJ/kg)$$

$$\Delta h = h_2 - h_1 \;=\; \int_1^2 C_p(T)\,dT \quad (kJ/kg)$$

- to carry out the above integrations, we need to know $C_v(T)$ and $C_p(T)$. These are available from a variety of sources

  **Table A-2a:** for various materials at a fixed temperature of $T = 300\ K$

  **Table A-2b:** various gases over a range of temperatures $250\ K \le T \le 1000\ K$

  **Table A-2c:** various common gases in the form of a third order polynomial

# Specific Heats: Ideal Gases

- for an ideal gas $Pv = RT$

$$C_v \;=\; \frac{du}{dT} \quad \Rightarrow \quad C_v = C_v(T)\ \ only$$

$$C_p \;=\; \frac{dh}{dT} \quad \Rightarrow \quad C_p = C_p(T)\ \ only$$

$$h = u + Pv \;\;\Rightarrow\;\; h = u + RT \;\;\Rightarrow RT = h(T) - u(T)$$

If we differentiate with respect to $T$

$$R = \frac{dh}{dT} - \frac{du}{dT}$$

$$\boxed{R = C_p - C_v}$$

# Specific Heats: Solids and Liquids

- solids and liquids are incompressible. (i.e., $\rho = constant$) and it can be shown (mathematically) that:

$$C_p = C_v = C$$

**Ideal gases:** $$\Delta u = \int_1^2 C(T)\, dT \approx C_{avg}\, \Delta T$$

$$\Delta h = \Delta u + \Delta(Pv) = \Delta u + v\Delta P + P\Delta \cancelto{0}{v}$$
$$\approx C_{avg}\Delta T + v\Delta P$$

**Solids:** $$\Delta h = \Delta u = C_{avg}\Delta T \quad (v\Delta P \text{ is negligible})$$

**Liquids:** If $P = const,\ \Delta h = C_{avg}\Delta T$

If $T = const,\ \Delta h = v\Delta P$

**Example 2-2:** Using water as the working fluid, complete the table shown below. Using graph paper, create a separate $T - v$ diagram for each state point that clearly shows how you have located the state point (approximately to scale). For instance, using State Point 1 as an example, show a curve of $T = 400\ °C$ and a curve of $P = 0.8\ MPa$. State Point 1 will be at the intersection of these two curves. The intersection should have the correct relationship to the vapor dome (i.e. inside or outside).

For each case, show all calculations necessary to establish the actual location of the state point. Identify the relevant charts or tables used to perform your calculations

In the table, under the column for quality ($x$), indicate the quality of the state point is under the dome, $CL$ if the state point is in the compressed liquid region and $SV$ if the state point is in the superheated vapor region.

| State | $T$ | $P$ | $v$ | $x$ |
|---|---|---|---|---|
| | $°C$ | $MPa$ | $m^3/kg$ | |
| 1 | 400 | 0.8 | | |
| 2 | 200 | | 0.005 | |
| 3 | | 3.5 | 0.05 | |
| 4 | | 0.01 | 20.0 | |
| 5 | | 0.2 | | 0.30 |
| 6 | 100 | 5.0 | | |
| 7 | 300 | | 0.5 | |
| 8 | 70.0 | | | 0.60 |
| 9 | 250 | 0.125 | | |