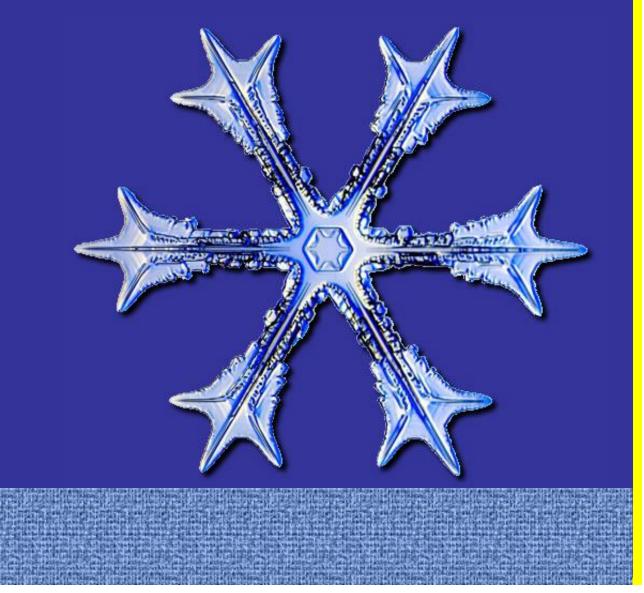
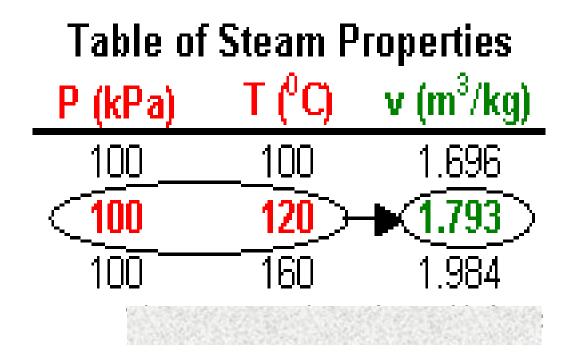
Thermodynamic Properties of Pure Substances



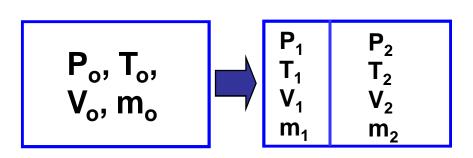
Any two independent intensive thermodynamic properties are sufficient to describe the state of a system containing a single pure substance.





Intensive and Extensive Properties

- The value of an extensive property is dependent of the mass of the system.
- The value of an intensive property is independent of the mass of the system.
- Partition box



$$P_0 = P_1 = P_2 \rightarrow \text{Intensive Prop}$$
$$T_0 = T_1 = T_2 \rightarrow \text{Intensive Prop}$$
$$V_0 \neq V_1 \neq V_2 \rightarrow \text{Extensive Prop}$$
$$m_0 \neq m_1 \neq m_2 \rightarrow \text{Extensive Prop}$$

• Try specific volume:

 $v = V/m \rightarrow v_0 = v_1 = v_2 \rightarrow Intensive Property$

ThermoNet

Intensive and Extensive Properties

Property	Extensive	Intensive
Mass	m	-
Temperature	-	Т
Pressure	-	Ρ
Volume	V	v = V/m (specific volume)
Internal Energy	U	u = U/m (<mark>specific</mark> internal energy)
Enthalpy	н	h = H/m (specific enthalpy)

• Any extensive property can be made intensive (specific) by dividing by mass.



Pure Substances

- Are composed of a single chemical species (e.g., either O₂ or CO₂ but not a mixture of O₂ and CO₂).
- May exist in more than one phase (e.g., solid and liquid)

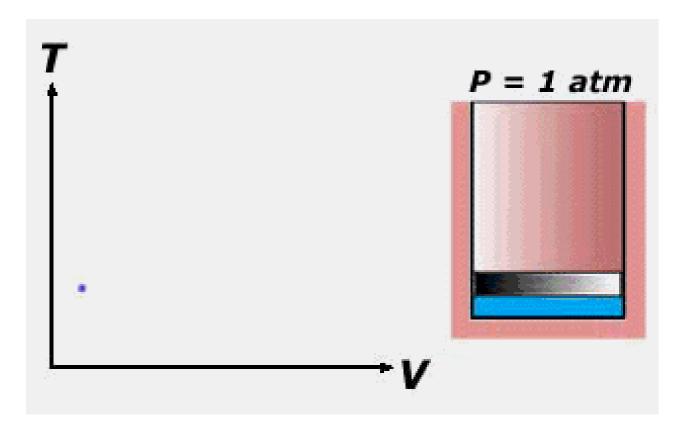
A mixture of snow, ice, liquid water and water vapor is a pure substance.





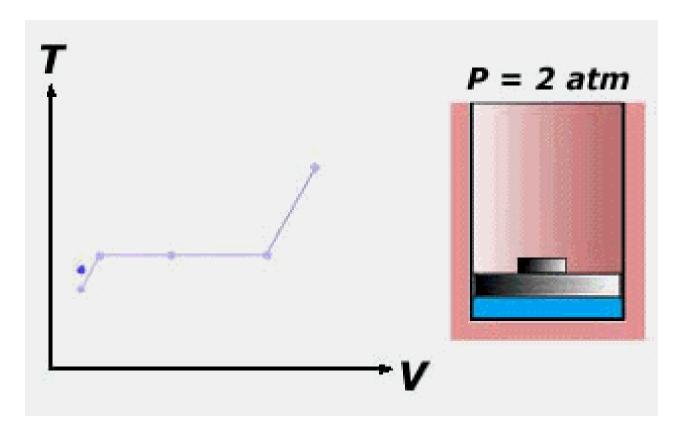
phase Change and P-v-T Surface

• Constant Pressure Heating in Piston-Cylinder at P = 1 atm



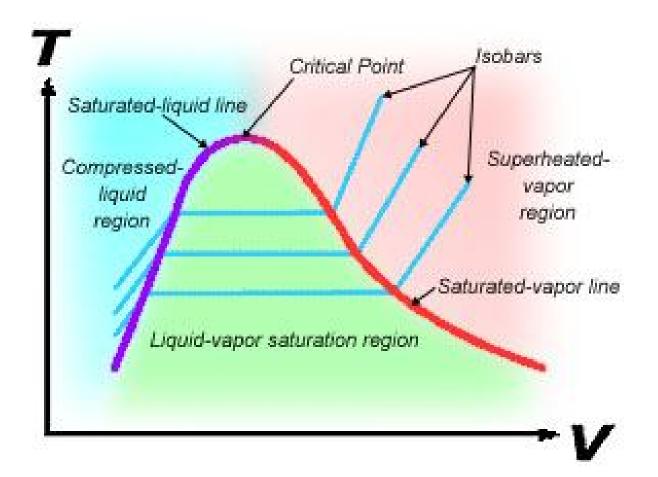


• Constant Pressure Heating in Piston-Cylinder at P = 2 atm

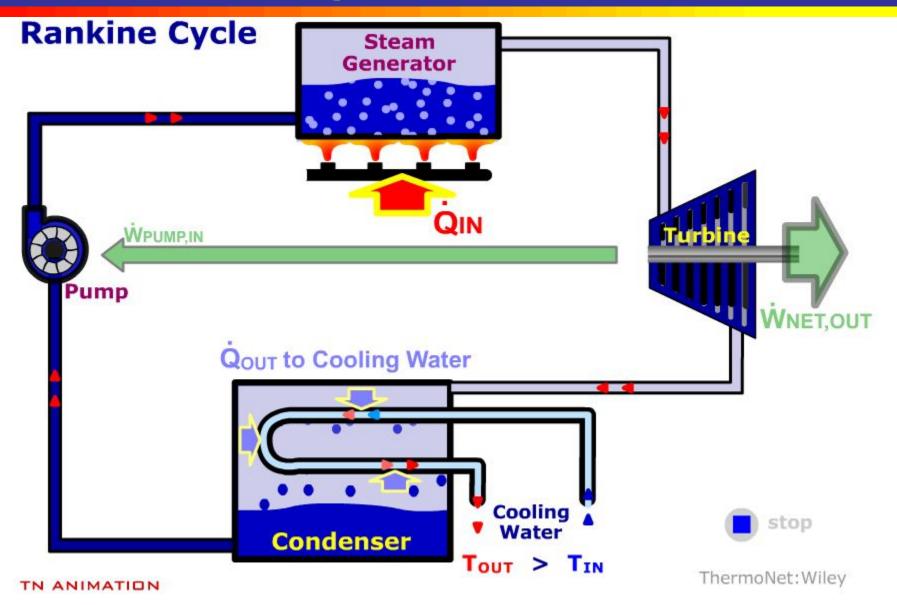




- Regions on T-v Diagram
- Note directions of Isobars

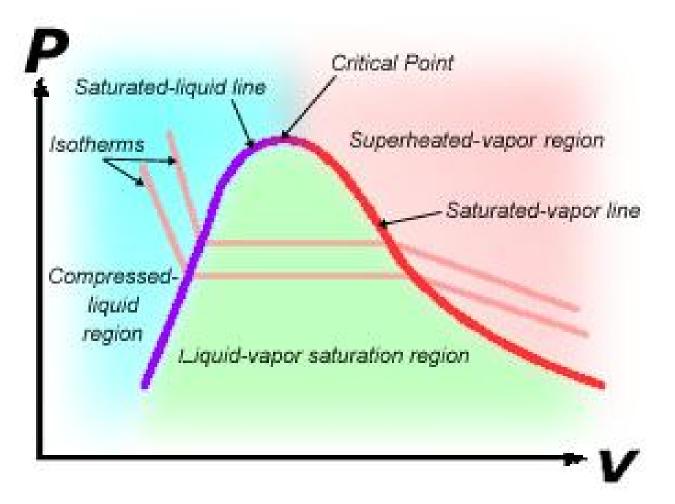






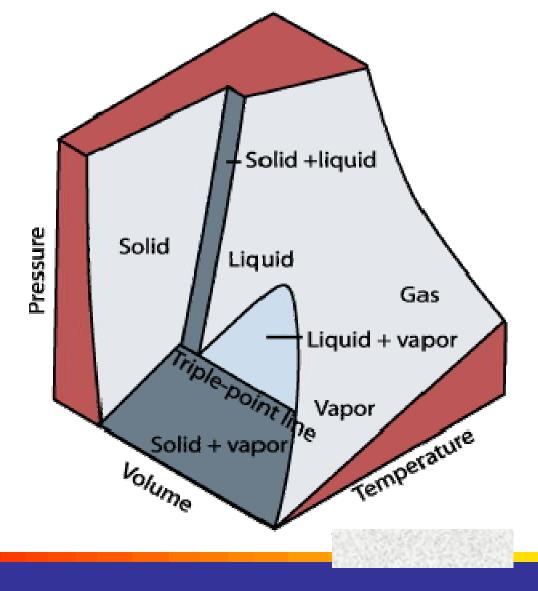


- Regions on P-v Diagram
- Note directions of Isotherms





• Three-Dimensional P-v-T Surface



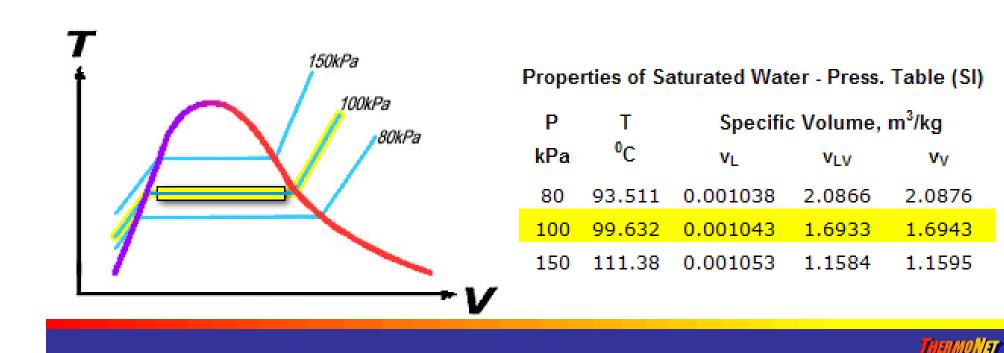


3.4 Liquid-Vapor Tables

- For Ideal Gases (treated later):
 - $-\mathbf{Pv} = \mathbf{RT}$
 - Very simple and accurate relation
- No similar relation exists for liquids, saturated liquid vapor mixtures or superheated vapors
- Typically superheated vapors do not obey the ideal gas law.
- Use data tabulated based on T and P
 - Compressed Liquid Tables
 - Saturated Liquid-Vapor Tables
 - Superheated Vapor Tables

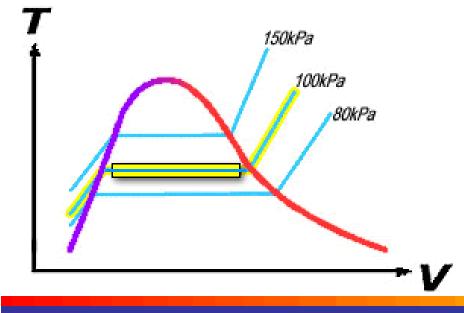


- **Property Notation (Subscripts):**
 - L = Saturated Liquid (e.g., v_L and u_L)
 - V = Saturated Vapor (e.g., v_v and u_v)
 - LV = Difference between saturated vapor and liquid values (e.g., v_{LV} = v_V - v_L)
 - SAT = Saturated Mixture (T_{SAT} and P_{SAT})



• Quality (x): Mass Fraction of Saturated Vapor

$$x = \frac{\text{mass of vapor}}{\text{total mass of mixture}} = \begin{pmatrix} \text{mass fraction} \\ \text{of vapor} \end{pmatrix}$$
$$1 - x = \frac{\text{mass of liquid}}{\text{total mass of mixture}} = \begin{pmatrix} \text{mass fraction} \\ \text{of liquid} \end{pmatrix}$$



Properties of Saturated Water - Press. Table (SI)

Ρ	Т	Specific Volume, m ³ /kg			
kPa	٥C	vL	VLV	vv	
80	93.511	0.001038	2.0866	2.0876	
100	99.632	0.001043	1.6933	1.6943	
150	111.38	0.001053	1.1584	1.1595	

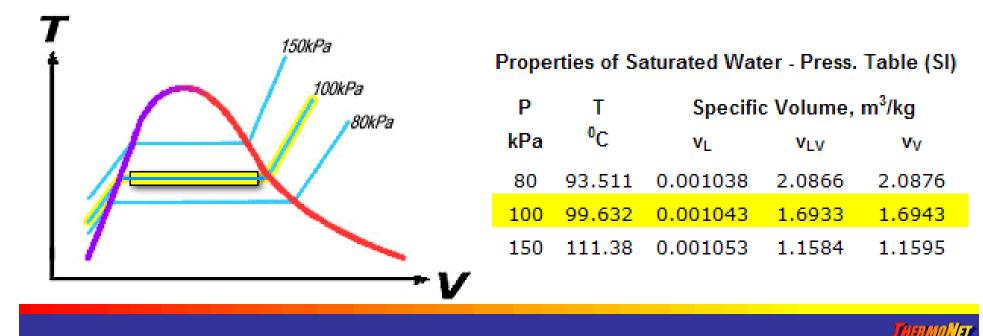
Thermoller

 Specific Volume (v) of Saturated Liquid Vapor Mixture with quality x

 $\mathbf{v} = \mathbf{v}_{L} + \mathbf{x}\mathbf{v}_{V}$

 Quality of Saturated Liquid Vapor Mixture with Specific Volume (v)

$$\mathbf{x} = \frac{\mathbf{v} - \mathbf{v}_{\mathsf{L}}}{\mathbf{v}_{\mathsf{V}} - \mathbf{v}_{\mathsf{L}}} = \frac{\mathbf{v} - \mathbf{v}_{\mathsf{L}}}{\mathbf{v}_{\mathsf{L}\mathsf{V}}}$$

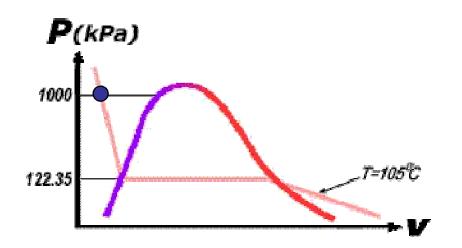


- Determine Phase if:
 - $P = 100 \text{ kPa and } v = 0.001000 \text{ m}^3/\text{kg}$
 - $P = 100 \text{ kPa and } T = 100^{\circ}C$
 - $P = 100 \text{ kPa and } v = 1.0000 \text{ m}^3/\text{kg}$

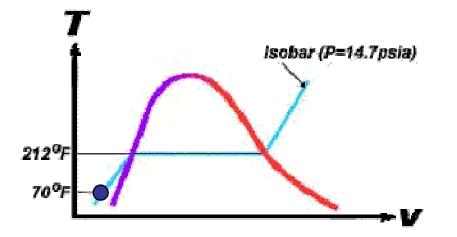
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3.6 Compressed (Subcooled) Liquids



- P = 1000 kPa & T = 105°C
- P_{SAT}(105^oC) = 122.35 kPa
 - Since P > P_{SAT}(T)
 - Compressed Liquid



- $T = 70^{\circ}F \& P = 14.7 psia$
- T_{SAT}(14.7 psia) = 212⁰F
 - Since T < T_{SAT}(P)
 - → Subcooled Liquid
- Subscript CL = Compressed Liquid: e.g., v_{CL}



3.6 Incompressible Liquid Approx (ICL)

- v_{CL}(70°C, 5000 kPa) = 0.001020 m³/kg
- $v_L(70^{\circ}C) = 0.00102 \text{ m}^3/\text{kg}$
- v_L(5000 kPa) = 0.00129 m³/kg
- $v_{CL}(T,P) \cong v_{L}(T) \rightarrow ICL$

Properties of Water in the Compressed Liquid State (SI) Р т h v u s m^3/kq kJ/kg kPa ٥C kJ/kg kJ/(kg·K) 5,000 0.001010 208.58 213.63 0.7014 50 70 0.001020 291.97 297.07 0.9520 ThermoNet: Wiley Properties of Saturated Water (SI) Specific Volume, m³/kg Internal Energy, kJ/kg Р т °c kPa VI. VLV ٧v uL ULV uγ 70 31.18 **0.00102** 5.0437 5.045 292.98 2175.8 2468.8 5000 0.00129 0.03815 0.039 1147.8 1448.7 2596.5 264

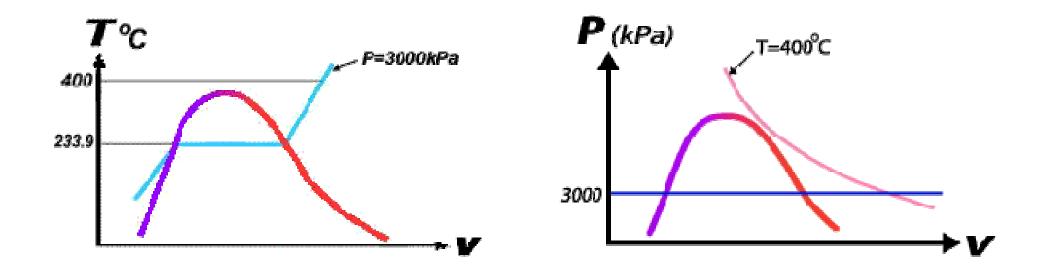


3.6 Incompressible Liquid Approx (ICL)

- $\mathbf{v}_{\mathsf{CL}}(T,P) \cong \mathbf{v}_{\mathsf{L}}(T)$
- $u_{CL}(T,P) \cong u_{L}(T)$
- $h_{CL}(T,P) \cong h_{L}(T) + v_{L}(T) [P P_{SAT}(T)]$
 - Recall $h = u + Pv \rightarrow h$ sensitive to P
 - $\text{ If } \mathsf{P} \cong \mathsf{P}_{\mathsf{SAT}}(T)$
 - \rightarrow h_L(T) >> V_L(T) [P P_{SAT}(T)]
 - \rightarrow h_{CL}(*T*,*P*) \cong h_L(*T*)



3.7 Superheated Vapor



T = 400°C & P = 3000 kPa T_{SAT} (3000 kPa) = 233.9°C Since T > T_{SAT}(P) → Superheated Vapor



3.7 Superheated Vapor

Properties of Water in the Superheated Vapor State (SI)						
Р	Т	v	u	h	S	
kPa	°C	m³/kg	kJ/kg	kJ/kg	kJ/(kg⋅K)	
200						
	(120.24)	(0.8859)	(2529.4)	(2706.5)	(7.1272)	
	150	0.9597	2576.7	2768.6	7.2793	
	200	1.0803	2653.9	2870.0	7.5059	
	250	1.1988	2730.8	2970.5	7.7078	
300						
	(133.56)	(0.6059)	(2543.5)	(2725.3)	(6.9921)	
	150	0.6339	2570.7	2760.9	7.0779	
	200	0.7163	2650.2	2865.1	7.3108	
	250	0.7963	2728.2	2967.1	7.5157	

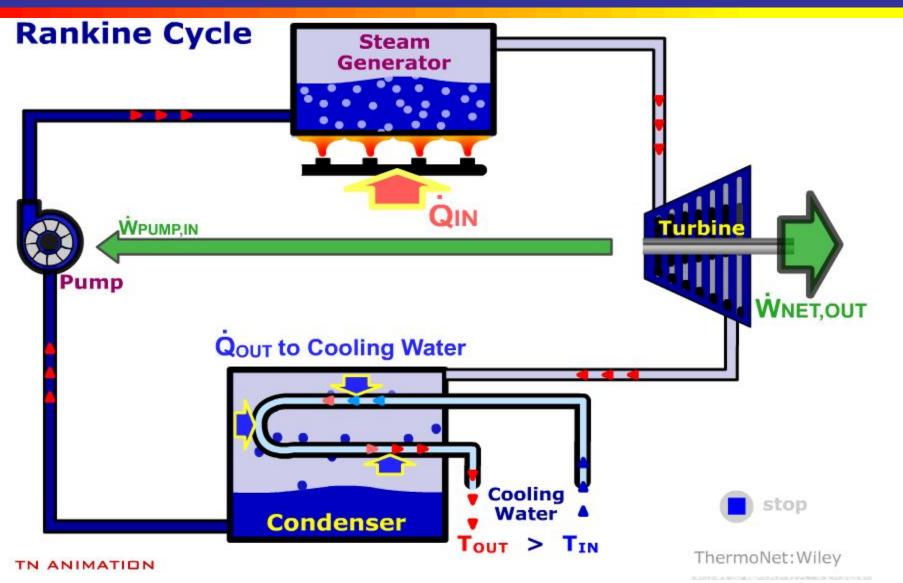


3.8 Gases

- Molecules are relatively far apart
- Do not feel one another's presence except during collisions
- Have a low density
- Are highly compressible
- In next two slides, compare
 - Liquid-Vapor working fluid in steam engine
 - Gas working fluid in gas turbine

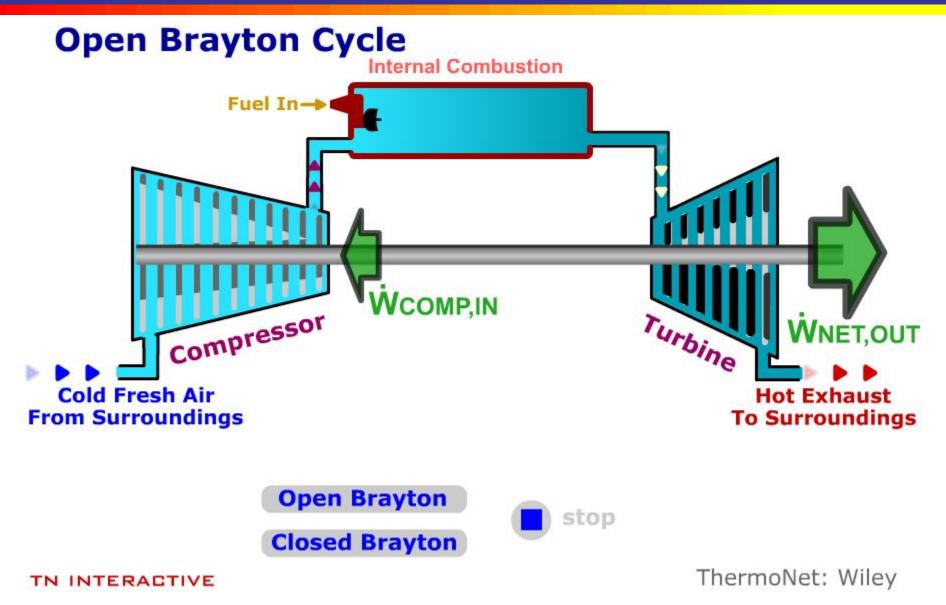


3.8 Gases



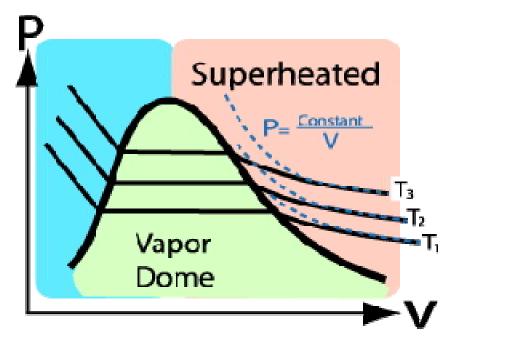








3.9 Ideal Gas Law



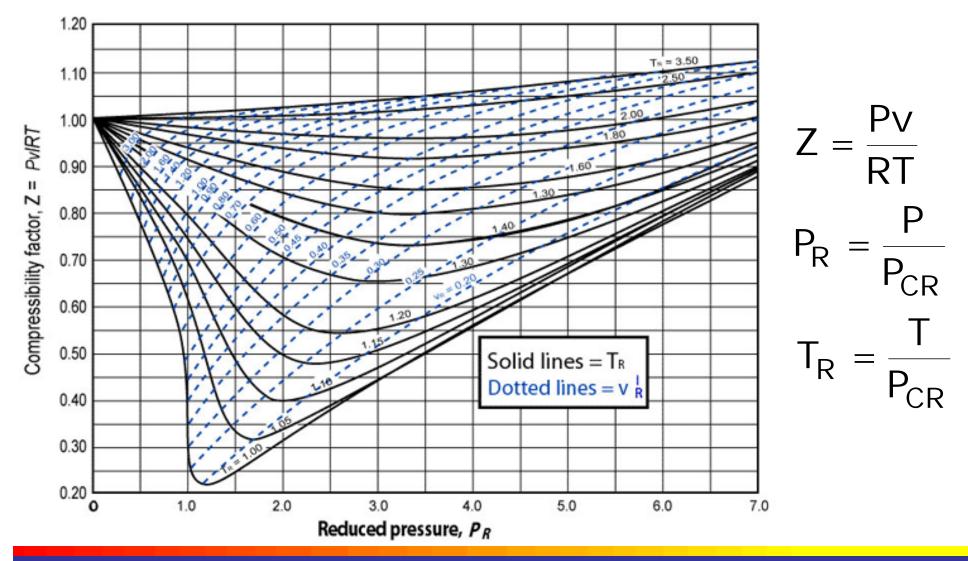
 $PV = n\overline{R}T \iff n = \frac{m}{M}$ $PV = \frac{m}{M}\overline{R}T \iff \overline{R} = RM$ $PV = mRT \iff v = \frac{V}{m}$ Pv = RT

- Universal Gas Constant (R): All gases have same value.
- Particular Gas Constant (R): Each gas has a unique value.



3.10 Compressibility Factor

• Use if not IGL and vapor tables not available



Thermoller

3.11 Other Equations of State

Van der Waals' equation

$$\mathsf{P} = \frac{\mathsf{RT}}{\mathsf{v} - \mathsf{b}} - \frac{\mathsf{a}}{\mathsf{v}^2}$$

Redlich-Kwong Equation

$$\mathsf{P} = \frac{\mathsf{RT}}{\mathsf{v} - \mathsf{b}_{\mathsf{RK}}} - \frac{\mathsf{a}_{\mathsf{RK}}}{\mathsf{v}\left(\mathsf{v} + \mathsf{b}_{\mathsf{RK}}\right)\mathsf{T}^{1/2}}$$

Benedict-Webb-Rubin Equation of State

$$\mathsf{P} = \frac{\mathsf{RT}}{\mathsf{v}} + (\mathsf{B}_0\mathsf{RT} - \mathsf{A}_0 - \frac{\mathsf{C}_0}{\mathsf{T}^2})\left(\frac{1}{\mathsf{v}^2}\right) + \frac{(\mathsf{b}\mathsf{RT} - \mathsf{a})}{\mathsf{v}^3} + \frac{\alpha \mathsf{a}}{\mathsf{v}^6} + \mathsf{c}\frac{1 + \gamma / \mathsf{v}^2}{\mathsf{v}^3\mathsf{T}^2}\exp\left(\frac{-\gamma}{\mathsf{v}^2}\right)$$

• Virial Equation of State

$$\mathsf{P} = \frac{\mathsf{RT}}{\mathsf{v}} \left(1 + \frac{\mathsf{B}}{\mathsf{v}} + \frac{\mathsf{C}}{\mathsf{v}^2} + \dots \right)$$



3.12 Internal Energy and Enthalpy

- Internal Energy
 - If not an ideal gas, u = u(T,P)
 - If ideal gas, $u = u(T) \neq u(P)$
- Enthalpy
 - Recall h = u + Pv
 - For an Ideal Gas, $Pv = RT \rightarrow h = u(T) + RT$
 - Therefore for ideal gas, $h = h(T) \neq h(P)$
- T, u and h are dependent properties for ideal gases



3.13 Heat Capacities and Specific Heats

• Approximately,

$$C = \frac{\Delta \text{ Energy}}{\Delta T}$$

 Heat capacity (C_v) and specific heat capacity (c_v) for constant volume process

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$
 and $c_v = \left(\frac{\partial u}{\partial T}\right)_v$

 Heat capacity (C_P) and specific heat capacity (C_P) for constant pressure process

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$
 and $c_P = \left(\frac{\partial h}{\partial T}\right)_P$



3.13 Specific Heats for Ideal Gases

• For an ideal gas, $h = h(T) \neq h(P)$ and

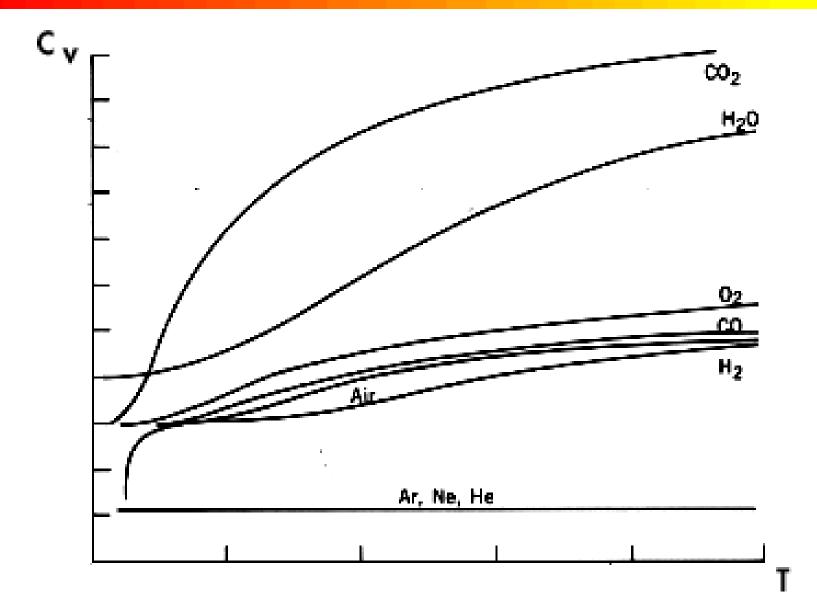
$$c_{P} = \left(\frac{\partial h}{\partial T}\right)_{P} = \frac{dh}{dT} \implies \Delta h = \int_{T_{1}}^{T_{2}} c_{P} dT \text{ Always}$$

• Similarly, for ideal gas $u = u(T) \neq u(V)$ and

$$c_V = \left(\frac{\partial u}{\partial T}\right)_V = \frac{du}{dT} \implies \Delta u = \int_{T_1}^{T_2} c_V dT$$
 Always



3.13 Specific Heats for Ideal Gases



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3.13 Specific Heats for Ideal Gases

$$\Delta u = \int_{T_1}^{T_2} c_V dT \qquad \Delta h = \int_{T_1}^{T_2} c_P dT$$

- $\mathbf{R} = \mathbf{c}_{\mathbf{P}} \mathbf{c}_{\mathbf{V}}$
- For monatomic gases (e.g., He, Ar, Ne)
 - $-c_v = 3R/2 = Constant$
 - $-c_{P} = 5R/2 = Constant$
- $\Delta u = c_v \Delta T$ only if $c_v = constant$
- $\Delta h = c_P \Delta T$ only if $c_P = constant$



3.13 Specific Heats for Solids and Liquids

• For incompressible solids and liquids,

- $-\mathbf{c}_{\mathsf{P}}=\mathbf{c}_{\mathsf{V}}$
- Sometimes denoted as c

$$\Delta u = \Delta h = \int_{T_1}^{T_2} c dT$$



3.14 Ideal Gas Tables

- Unlike steam tables, pressure not tabulated
- Use Pv = RT to relate P, v and T
- Use tables to relate T, u and h



3.15 Some Other Thermodynamic Properties

Isothermal Compressibility (k)

$$\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_{T}$$

Coefficient of Thermal Expansion (b)

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_{P}$$

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

• Joule Thompson Coefficient (m)

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

