Unit one – Properties of Pure Substances

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Mechanical Engineering 370

Thermodynamics

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California State University Northridge

Outline

- Extensive, E, m, intensive, T, P, ρ, and specific, e = E/m, variables
- ρ = m/V = 1/v => density = 1/(sp. vol.)
- Look at P-v-T data for real substances
- Ideal gases $PV = nR_uT = mRT$
  - Engineering gas constant: $R = R_u / M$
  - With v = V/m, Pv = RT
    - Use of V or v = V/m gives difference between PV = mRT and Pv = RT

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Thermodynamic Variables

- Extensive variables (volume, mass, energy) depend on size of system
- Intensive variables (pressure, temperature, density) do not
- Specific variables are ratio of an extensive variable to mass (e.g. specific volume, v = V/m)
- General notation, if E is an extensive variable, e = E/m is specific variable

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Thermodynamic System

- Basic unit of analysis defined by boundaries where all interactions occur
- State of system defined by properties
- Interaction of system with surroundings
  - Can interchange energy and mass
  - Open/closed systems: Have/Do not have mass addition or removal
    - Open system called control volume
  - Isolated system: constant energy and mass
  - All interactions across boundaries

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Thermodynamic State

- Two independent intensive properties determine the state of a simple compressible system
- Once the state of a system is deter-mined all other properties are known
- Thermodynamic processes are a continuous series of states known as a quasi-equilibrium process

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Ideal Gas Equations

- From chemistry: $PV = nR_uT$
- R_u = Universal gas constant = 8.314 kJ/kmol·K = 8.314 kPa · m^3/kmol·K = 10.73 psia ·ft^3/lbmol ·K
- Engineering gas constant, $R = R_u/M$
- Definition of mol, n = m / M
- PV = (m/M)(MR)T = mRT
- P(V/m) = Pv = RT

$PV = nR_uT$

$PV = mRT$

$Pv = RT$

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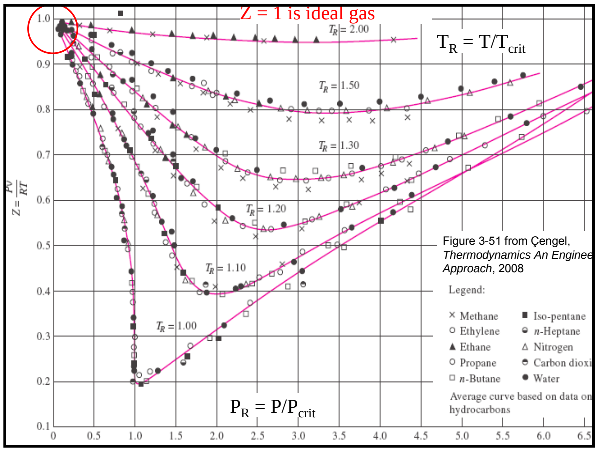

Why Use Ideal Gas?

- Simple equations
- Real gas behavior close to ideal gas for low pressure (or high temperature)
- Want P low compared to P_c
- Example calculation: find specific volume of water at 1,000°C and 10 kPa
- Compare to property table value of v = 58.758 m³/kg for water (page 918)

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Finding R

908 PROPERTY TABLES AND CHARTS

TABLE A–1

Molar mass, gas constant, and critical-point properties

1kJ = 1 kN·m = 1 (kN/m²)·m³ = 1 KPa·m³

Substance	Formula	Molar mass, M kg/kmol	Gas constant, R kJ/kg·K*
Air	—	28.97	0.2870
Ammonia	NH_3	17.03	0.4882
Argon	Ar	39.948	0.2081
Benzene	C_6H_6	78.115	0.1064
Bromine	Br_2	159.808	0.0520
Trichlorofluoromethane (R-11)	CCl_3F	137.37	0.06052
Water	H_2O	18.015	0.4615
Xenon	Xe	131.30	0.06332

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Ideal Gas Calculation

- Table A-1, page 908: for water, R = 0.4615 kJ/kg·K = 0.4615 kPa·m³/kg·K

$$v = \frac{RT}{P} = \frac{\frac{0.4615\ kPa \cdot m^3}{kg \cdot K}(1273.15\ K)}{10\ kPa} = \frac{58.756\ m^3}{kg}$$

- Error is only 0.0017% at this point
- Ideal gas often used for "permanent gases" such as air

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Ideal Gas Calculation II

- A volume of 20 ft³ at a pressure of 300 psia contains 20 lb_m of Helium; what is the temperature?
- T = PV / (mR)
- R = 2.6809 psia•ft³/lb_m•R (page 958)

$$T = \frac{PV}{mR} = \frac{(300\ psia)(20\ ft^3)}{(20\ lb_m)\frac{2.6809\ psia \cdot ft^3}{lb_m \cdot R}} = 111.9\ R = -347.7^o F$$

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P-v-T for Real Substances

- Three phases: gas, liquid and solid
- Look at gas and liquid
- Thought experiment
  - Add heat to a liquid at constant pressure; measure T and v
  - After a while vapor starts to form
    - Heat addition increases volume by converting liquid to gas while T is constant (at constant P)
  - Finally have only gas that expands readily
    - Ideal gas has v/T = const (at constant P)

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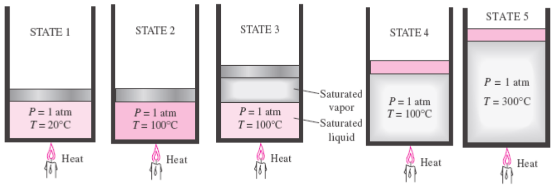
Thought Experiment II



- States 2 to 4 are liquid vapor transition
  - Liquid and vapor have same properties (P, $v_f = 1/\rho_f$, $v_g = 1/\rho_g$, and T) during transition; only relative proportions change

Figures 3-6 to 3-10 from Çengel, *Thermodynamics An Engineering Approach*, 2008

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Thought Experiment III

- Repeat experiment with difference in variables
- Hold temperature constant
- Add heat and measure pressure, P, and specific volume v
- Have same liquid-vapor transition
  - P is constant if T is constant
  - Liquid and vapor properties constant in transition only relative proportions change

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Thought Experiment Results

- A constant temperature line on P-v
  - Looks like a hyperbola in the gas region
  - Has constant pressure during the transition from liquid to gas
  - Is nearly vertical in the liquid region
- The points where the transition between liquid and gas take place for different temperatures: saturation curve
- Results of "experiment" on next slide

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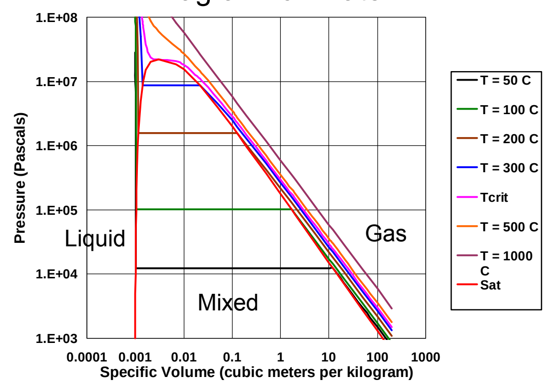
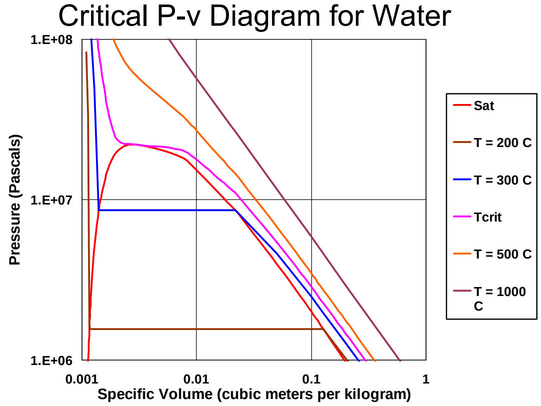
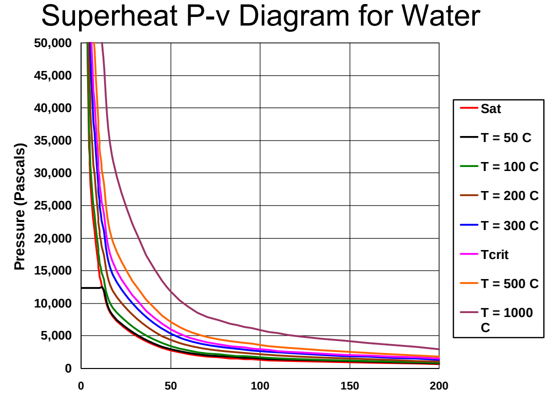
P-v Diagram for Water



Critical P-v Diagram for Water



Superheat P-v Diagram for Water



What We Have to Do

- Find all intensive thermodynamic properties when we are given only two intensive properties
  - Two independent, intensive properties define state
- Here we will discuss only four intensive properties, P, v, T, and fraction of vapor in mixed region called the quality, x
- Approach used here will be applied to finding other properties: internal energy, enthalpy, and entropy

Finding Properties

- When we have a mixture of liquid and gas T and P are not independent
- For a single phase (liquid or gas) T and P are independent (can specify state)
- In the mixed region we use vapor mass fraction, called quality, x

$$x \equiv \frac{m_g}{m_g + m_f} = \frac{v - v_f}{v_g - v_f} = \frac{v - v_f}{v_{fg}}$$

- v_f and v_g are found from either T or P

Quality Derived

- Mixed region volume is sum of liquid and vapor volumes

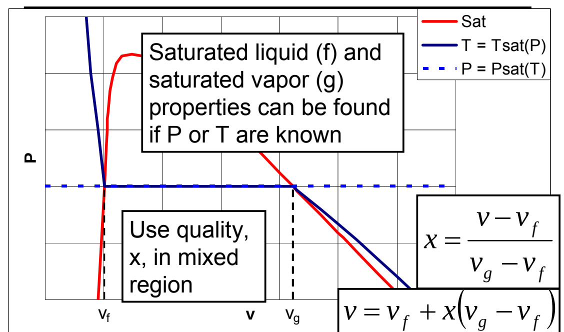
$$V = m_g v_g + m_f v_f \quad \Rightarrow \quad \frac{V}{m} = \frac{m_g}{m} v_g + \frac{m_f}{m} v_f = \frac{m_g}{m} v_g + \frac{m - m_g}{m} v_f$$

- Use quality: $x = m_g/(m_g + m_f) = m_g/m$

$$v = \frac{V}{m} = \frac{m_g}{m} v_g + \frac{m - m_g}{m} v_f = x v_g + (1 - x) v_f = v_f + x\left(v_g - v_f\right)$$

- Will apply this later to other properties

Saturation Properties



Saturation Tables

- See steam tables, pp 914–923
- Saturation tables
  - Table A-4 has T as lookup variable
  - Table A-5 has P as lookup variable
  - Same results in each table
- Other variables besides specific volume have saturated liquid ($_f$) and gas ($_g$)
- Example: what are P and v if T = 220°C and x = 0.25?

Saturated water—Temperature table (Continued)

		Specific volume, m³/kg		Internal energy, kJ/kg		
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
205	1724.3	0.001164	0.11508	872.86	1723.5	2596.
210	1907.7	0.001173	0.10429	895.38	1702.9	2598.
215	2105.9	0.001181	0.094680	918.02	1681.9	2599.
220	2319.6	0.001190	0.086094	940.79	1660.5	2601.
225	2549.7	0.001199	0.078405	963.70	1638.6	2602.

- Use Table A-4, Page 915, T = 220°C
- Find P = 2319.6 kPa, v_f = 0.001190 m³/kg and v_g = 0.086094 m³/kg

What is v for x = 0.25?

- Found from Table A-4 with lookup T
  - $P = P_{sat}(T = 220^oC) = 2319.6$ kPa
  - $v_f(T = 220^oC) = 0.001190$ m^3/kg
  - $v_g(T = 220^oC) = 0.086094$ m^3/kg

$$x = \frac{v - v_f}{v_g - v_f} \quad \Leftrightarrow \quad v = v_f + x(v_g - v_f) = (1-x)v_f + xv_g$$

$$v = (1-x)v_f + xv_g = (1-0.25)\frac{0.001190\ m^3}{kg} + (0.25)\frac{0.086094\ m^3}{kg}$$

$$v = \frac{0.022416\ m^3}{kg}$$

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What if P and T are Given?

- If these are independent properties then they define a state
- The "superheat" (gas) tables for water (Table A-6, pp 918 – 921) have a set of tables for P with rows of data for v
- Data are also given for other properties
- Basic question: Given T and P, how do we know if we have a liquid or a gas?

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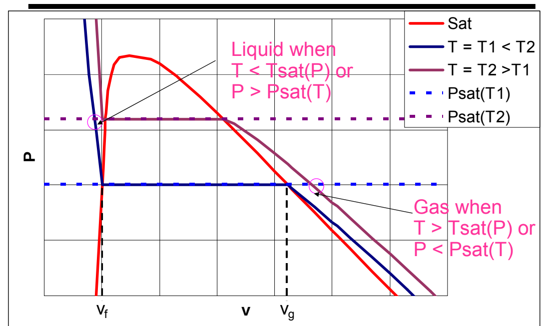
TABLE A–6

Superheated water

T °C	v m^3/kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m^3/kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m^3/kg	u kJ/kg	h kJ/kg
	P = 0.01 MPa (45.81°C)*				P = 0.05 MPa (81.32°C)				P = 0.10 MPa (99.6		
Sat.†	14.670	2437.2	2583.9	8.1488	3.2403	2483.2	2645.2	7.5931	1.6941	2505.6	2675.
50	14.867	2443.3	2592.0	8.1741							
100	17.196	2515.5	2687.5	8.4489	3.4187	2511.5	2682.4	7.6953	1.6959	2506.2	2675.
150	19.513	2587.9	2783.0	8.6893	3.8897	2585.7	2780.2	7.9413	1.9367	2582.9	2776.
200	21.826	2661.4	2879.6	8.9049	4.3562	2660.0	2877.8	8.1592	2.1724	2658.2	2875.
250	24.136	2736.1	2977.5	9.1015	4.8206	2735.1	2976.2	8.3568	2.4062	2733.9	2974.
300	26.446	2812.3	3076.7	9.2827	5.2841	2811.6	3075.8	8.5387	2.6389	2810.7	3074.
400	31.063	2969.3	3280.0	9.6094	6.2094	2968.9	3279.3	8.8659	3.1027	2968.3	3278.
500	35.680	3132.9	3489.7	9.8998	7.1338	3132.6	3489.3	9.1566	3.5655	3132.2	3488.
600	40.296	3303.3	3706.3	10.1631	8.0577	3303.1	3706.0	9.4201	4.0279	3302.8	3705.
700	44.911	3480.8	3929.9	10.4056	8.9813	3480.6	3929.7	9.6626	4.4900	3480.4	3929.
800	49.527	3665.4	4160.6	10.6312	9.9047	3665.2	4160.4	9.8883	4.9519	3665.0	4160.
900	54.143	3856.9	4398.3	10.8429	10.8280	3856.8	4398.2	10.1000	5.4137	3856.7	4398.
1000	58.758	4055.3	4642.8	11.0429	11.7513	4055.2	4642.7	10.3000	5.8755	4055.0	4642.
1100	63.373	4260.0	4893.8	11.2326	12.6745	4259.9	4893.7	10.4897	6.3372	4259.8	4893.
1200	67.989	4470.9	5150.8	11.4132	13.5977	4470.8	5150.7	10.6704	6.7988	4470.7	5150.
1300	72.604	4687.4	5413.4	11.5857	14.5209	4687.3	5413.3	10.8429	7.2605	4687.2	5413.
	P = 0.20 MPa (120.21°C)				P = 0.30 MPa (133.52°C)				P = 0.40 MPa (143.6		
Sat.	0.88578	2529.1	2706.3	7.1270	0.60582	2543.2	2724.9	6.9917	0.46242	2553.1	2738.
150	0.95986	2577.1	2769.1	7.2810	0.63402	2571.0	2761.2	7.0792	0.47088	2564.4	2752.
200	1.08049	2654.6	2870.7	7.5081	0.71643	2651.0	2865.9	7.3132	0.53434	2647.2	2860.

Finding State with Given T and P



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General Rules

- When we are given T and P we have a single phase. Is it gas or liquid?
  - It is a gas if $T > T_{sat}(P)$ or $P < P_{sat}(T)$
  - It is a liquid if $T < T_{sat}(P)$ or $P > P_{sat}(T)$
  - "Superheat" tables have T_{sat} by P
  - Can guess superheat and check
    - Example: R134a at 0°C and P = 100 kPa, 400 kPa
    - Guess superheat and find at 100 kPa and 0°C, v = 0.21630 m^3/kg; at 400 kPa there is no 0°C entry
    - Data from page 929

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perheated refrigerant-134a

	v m^3/kg	u kJ/kg	h kJ/kg	s kJ/kg · K	v m^3/kg	u kJ/kg	h kJ/kg
	P = 0.06 MPa (T_{sat} = −36.95°C)				P = 0.10 MPa (T_{sat} = −2		
t.	0.31121	209.12	227.79	0.9644	0.19254	215.19	234.44
20	0.33608	220.60	240.76	1.0174	0.19841	219.66	239.50
10	0.35048	227.55	248.58	1.0477	0.20743	226.75	247.49
0	0.36476	234.66	256.54	1.0774	0.21630	233.95	255.58
10	0.37893	241.92	264.66	1.1066	0.22506	241.30	263.81
20	0.39302	249.35	272.94	1.1353	0.23373	248.79	272.17
30	0.40705	256.95	281.37	1.1636	0.24233	256.44	280.68
40	0.42102	264.71	289.97	1.1915	0.25088	264.25	289.34
50	0.43495	272.64	298.74	1.2191	0.25937	272.22	298.16
60	0.44883	280.73	307.66	1.2463	0.26783	280.35	307.13
70	0.46269	288.99	316.75	1.2732	0.27626	288.64	316.26
80	0.47651	297.41	326.00	1.2997	0.28465	297.08	325.55
90	0.49032	306.00	335.42	1.3260	0.29303	305.69	334.99
00	0.50410	314.74	344.99	1.3520	0.30138	314.46	344.60

Results

- v(0°C, 100 kPa) = 0.21630 m³/kg
- What is v(0°C, 100 kPa)? Page 929

P = 0.40 MPa (T_{sat} = 8.91°C)

Sat.	0.051201	235.07	255.55	0.9269
0				
10	0.051506	235.97	256.58	0.9305
20	0.054213	244.18	265.86	0.9628
30	0.056796	252.36	275.07	0.9937

- Why are there no data at T = 0°C and P = 400 MPa (= 0.4 MPa)?

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General Rules Continued

- The example did not find a 0°C entry at 400 kPa because this is a liquid
  - The header 0.4 MPa (T_{sat} = 8.91°C confirms that T = 0°C < T_{sat} = 8.91°C
- Approximation for compressed liquid: $v(T,P) \approx v_f(T)$ Note it's $v_f(\boldsymbol{T})$
  - To get answer for 400 kPa and 0°C look at saturation table for T = 0°C, A-11, page 926
  - $v(0°C, 400\ kPa) \approx v_f(0°C)$ = 0.0007723 m³/kg

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Two More Problems

- What is the specific volume for refrigerant 134a (R-134a) when the pressure is 90 psia and the temperature is 240°F
  - R-134a tables in english units: pp. 976-979
  - Guess that this is gas and look in "superheated" tables on page 979
  - v = 0.77796 ft³/lb_m at given T and P
- What is P when T = 240°F and v = 0.77796 ft³/lb_m?

90 psia

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Review Last Problem

- What is the specific volume for refrigerant 134a (R-134a) when the pressure is 90 psia and the temperature is 240°F
  - R-134a tables in english units: pp. 978-81
  - What if we could not guess that this is gas or made a wrong guess?
    - Use general rule that gas occurs when $P < P_{sat}(T)$ or $T > T_{sat}(P)$
    - For this problem T = 240°F > T_{sat}(90 psia) = 72.83°F
    - Also P = 90 psia < P_{sat}(240°F) = 138.79 psia

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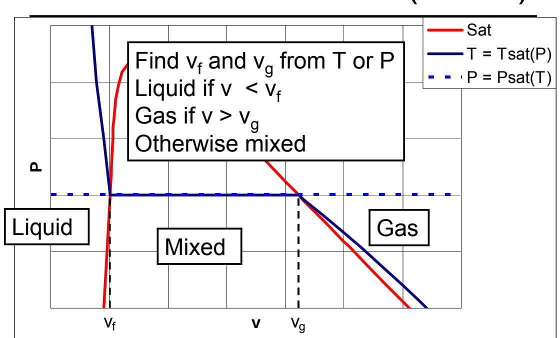
Find State Given v and (T or P)



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Given T-v(or P-v); Find P(or T)

- Determine state: find v_f and v_g from saturation tables for given T (or P)
  - If v > v_g it is a gas; use superheat table
  - If v < v_f it is a liquid; see below
  - If v_f < v < v_g it is in mixed region. Can find x
- For liquid to use $v \approx v_f(T)$ we must be given v-P: find T for which $v_f(T) = v_{given}$
- Compressed liquid tables for water

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Interpolation

- Can use interpolation function on your calculator if you have one
- Basic idea is that you have a table with data pairs (x_1, y_1) and (x_2, y_2)
- You want to find a value of y for some value of x between x_1 and x_2
- Simplest idea is to assume a straight line between x_1 and x_2

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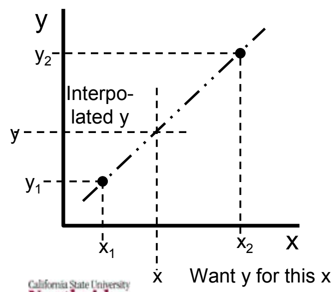
Interpolation II



- For a straight line any two points on the line can give slope

$$\frac{y_2 - y_1}{x_2 - x_1} = \frac{y - y_1}{x - x_1}$$

$$y = y_1 + \frac{y_2 - y_1}{x_2 - x_1}(x - x_1)$$

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Interpolation III

- Equation for a straight line between data pairs (x_1, y_1) and (x_2, y_2) is

$$y = y_1 + \frac{y_2 - y_1}{x_2 - x_1}(x - x_1) \quad or \quad \frac{y - y_1}{x - x_1} = \frac{y_2 - y_1}{x_2 - x_1}$$

- Second form is easier to remember
  - It says that the slope between any point (x,y) and the point (x_1, y_1) is the same as the slope between (x_1, y_1) and (x_2, y_2)
- First form used for computations

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Example Problem

- For H_2O at P = 2 MPa, what is T when v(m^3/kg) = (a) 0.00115, (b) 0.01, (c)0.2?
- Table A-5, p 917 At 2000 kPa, v_f = 0.001177 m^3/kg, v_g = 0.099587 m^3/kg
  - Thus (a) is liquid, (b) is mixed, (c) is gas
- For compressed liquid state (a), correct T is one for which v_f(T)= 0.00115 m^3/kg
  - Extract from Table A-4, next slide, shows that this v_f is between T = 195°C and T = 200°C

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Data and Interpolation

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TABLE A–4

Saturated water—Temperatu

Speci

Temp., T °C	Sat. press., P_{sat} kPa	Sat. liquid, v_f
195	1398.8	0.001149
200	1554.9	0.001157

- We want to find T for v = 0.00115 m^3/kg
  - Between 195°C and 200°C
- For this interpolation x_1 = 0.001149 m^3/kg, x_2 = 0.001157 m^3/kg, y_1 = 195°C and y_2 = 200°C

$$T = 195^\circ C + \frac{200^\circ C - 195^\circ C}{.001157\, m^3/kg - .001149\, m^3/kg}\left(.00115\, m^3/kg - .001149\, m^3/kg\right) = 195.6^\circ C$$

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Example: (b) Mixed, (c) Gas

- (b) for mixed region, T = T_{sat}(2 Mpa) = 212.38°C; can find quality

$$x = \frac{v - v_f}{v_g - v_f} = \frac{.01\, m^3/kg - .001177\, m^3/kg}{.099587\, m^3/kg - .001177\, m^3/kg} = 0.0896 = 8.96\%$$

- (c) v = .2 m^3/kg at P = 2 MPa found on p. 921 between T = 600°C and 700°C

$$T = 600^\circ C + \frac{700^\circ C - 600^\circ C}{.22326\, m^3/kg - .19962\, m^3/kg}\left(.2\, m^3/kg - .19962\, m^3/kg\right) = 601.6^\circ C$$

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Compressed Liquid Table

- Not a common table, use here to check approximation that $v(P,T) \approx v_f(T)$
- Table A-7, page 922, gives v(50 MPa, 100°C) = 0.0010201 m³/kg
- Table A-4, page 914, gives v_f(100°C) = 0.001043 m³/kg
- Error is about 2% even for a pressure difference of 49.9 MPa between the actual pressure and saturation pressure

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More on Compressed Liquid

- Check approximation that $v(P,T) \approx v_f(T)$ for previous problem: v = 0.00115 m³/kg and P = 2 MPa
- Do not have data for compressed liquid at 2 MPa in table on page 922
  - First entry is at 5 MPa
- Have to use double interpolation and interpolation with saturation points
  - Interpolate between P_{sat} and 5 MPa

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Interpolations

- We are looking for v = 0.00115 m³/kg which is between 180°C and 200°C in compressed liquid table at 5 MPa
- We have to find data at these temperatures and 2 MPa
  - Because 5 MPa is the first table entry we use saturation as the lower data point
    - $v_f(T) = v(T, P_{sat})$

$$v(T, 2\,MPa) = v_f(T) + \frac{v(T, 5\,MPa) - v_f(T)}{5\,MPa - P_{sat}(T)}\left[2\,MPa - P_{sat}(T)\right]$$

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Table

2 MPa — P = 5 MPa (263.94°C

T °C	v m³/kg	u kJ/kg	h kJ/kg
Sat.	0.0012862	1148.1	1154.5
0	0.0009977	0.04	5.03
20	0.0009996	83.61	88.61
40	0.0010057	166.92	171.95
60	0.0010149	250.29	255.36
80	0.0010267	333.82	338.96
100	0.0010410	417.65	422.85
120	0.0010576	501.91	507.19
140	0.0010769	586.80	592.18
160	0.0010988	672.55	678.04
180	0.0011240	759.47	765.09
200	0.0011531	847.92	853.68

Compressed liquid data shown here

Looking for v = 0.00115 m³/kg at P = 2 MPa

No data for P < 5 M Pa

Use saturated liquid data for lower pressure

At 180°C, v_f = 0.001127 m³/kg at P = 1.0021 MPa

At 200°C, v_f = 0.001157 m³/kg at P = 1.5538 MPa

Interpolate to get v at 2 MPa at 180°C, 200°C

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Interpolations II

- Apply formula for T = 180°C and 200°C

$$v(180^oC, 2\,MPa) = .001127\,m^3/kg + \frac{.001125\,m^3/kg - .001127\,m^3/kg}{5\,MPa - 1.0021\,MPa}(2\,MPa - 1.0021\,MPa) = \frac{.001126501\,m^3}{kg}$$

$$v(200^oC, 2\,MPa) = .001157\,m^3/kg + \frac{.001153\,m^3/kg - .001157\,m^3/kg}{5\,MPa - 1.5538\,MPa}(2\,MPa - 1.5538\,MPa) = \frac{.00115648\,m^3}{kg}$$

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Interpolations III

- Now interpolate between results for two different T's to find T at desired v

$$T = 180^oC + \frac{200^oC - 180^oC}{\frac{.00115648\,m^3}{kg} - \frac{.001126501\,m^3}{kg}}\left(\frac{.00115\,m^3}{kg} - \frac{.001126501\,m^3}{kg}\right) = 195.7^oC$$

- Previous result using $v(T,P) \approx v_f(T)$ was 195.6°C

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