

0905322- Chemical Engineering Thermodynamics I Lecture 5: Properties of Pure Substances

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Outline

- Pure Substances
- OPvT behavior of pure substances
- ○Phase Diagrams (PvT, PT, Pv, Tv)
- Meaning of the Equilibrium Curves
 - o Clapeyron Equation
 - o Clausius-Clapeyron Equation
 - o Pitzer's Acentric Factor: Definition
- ○Quality
- Reference State and Reference Values



Pure Substances

- Pure substance: A substance that has a fixed chemical composition throughout.
 - Air is a mixture of several gases, but it is considered to be a pure substance.



FIGURE 3-1 Nitrogen and gaseous air are pure substances.

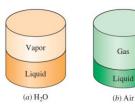


FIGURE 3-2
A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.



Phases of a Pure Substance

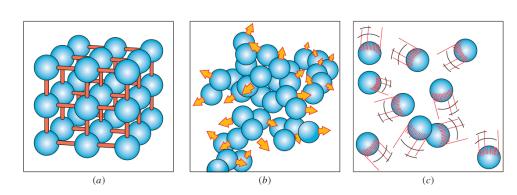


FIGURE 3-4

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.

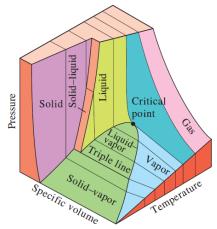


What Defines a Phase?

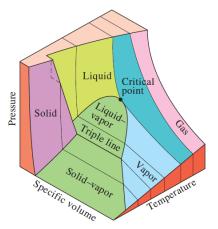
- A phase is considered a liquid if vaporization results from an isothermal pressure reduction (expansion).
- A phase is considered a gas if condensation results from isobaric temperature reduction (cooling).
 - \circ A **vapor** is a gas a temperature $T < T_c$ that can be **condensed** either
 - o by isothermal compression, or
 - o by isobaric cooling.
- Beyond the critical point, neither condensation nor vaporization leads to phase change, for which the phase is called a fluid.
 - \circ The region for which $T > T_c$ is termed the **supercritical** region.



PvTPhase Diagram



P-v-T surface of a substance that c*ontracts* upon freezing.



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



PT Phase Diagram



For water at the triple point $T_{\rm tp}$ = 0.01°C $P_{\rm tp}$ = 0.6117 kPa

For water at the normal boiling point

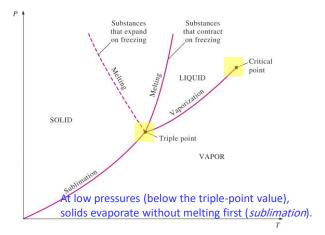
 $T_{\rm nb} = 99.97^{\circ}{\rm C}$

 $P_{\rm nb} = 101.325 \text{ kPa}$

For water at the critical point

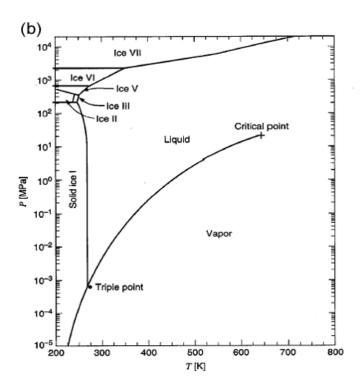
 $T_{c} = 373.95^{\circ}C$

 $P_c = 22.06 \text{ MPa}$





Pressure-Temperature diagrams for water





Saturation Temperature and Saturation Pressure

- oThe temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.
- OWater boils at 100°C at 1 atm pressure.
- \circ 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.

Saturation P/T can be synonyms with vaporization – melting – sublimation i.e., vapor pressure or melting pressure or sublimation pressure all are lumped into saturation pressure.



EXAMPLE 3-1 Pressure of Saturated Liquid in a Tank

A rigid tank contains 50 kg of saturated liquid water at 90°C. Determine the pressure in the tank and the volume of the tank.

SOLUTION A rigid tank contains saturated liquid water. The pressure and volume of the tank are to be determined.

Analysis The state of the saturated liquid water is shown on a T-U diagram in Fig. 3–28. Since saturation conditions exist in the tank, the pressure must be the saturation pressure at 90° C:

$$P = P_{\text{sat } @ 90^{\circ}\text{C}} = 70.183 \text{ kPa}$$
 (Table A-4)

The specific volume of the saturated liquid at 90°C is

$$U = U_{f@90^{\circ}C} = 0.001036 \text{ m}^{3}/\text{kg}$$
 (Table A-4)

Then the total volume of the tank becomes

$$V = mv = (50 \text{ kg})(0.001036 \text{ m}^3/\text{kg}) = 0.0518 \text{ m}^3$$

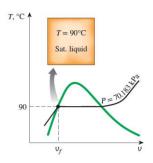


FIGURE 3–28
Schematic and *T-U* diagram for Example 3–1.



Meaning of the Equilibrium Curves

- The slope of the vapor-liquid equilibrium (VLE) curve gives the rate of change of the vapor pressure of the liquid with temperature.
- oThe slope of the **vapor-solid** coexistence curve is equal to the change of the vapor pressure of the solid (**sublimation pressure**) with temperature.
- oThe inverse of the slope of the **liquid-solid** coexistence line gives the **change of the melting temperature** of the solid with pressure.
- OAt equilibrium, the Clapeyron equation is:

$$\left(\frac{\partial P^{\text{sat}}}{\partial T}\right)_{g^I = g^{II}} = \frac{\Delta s}{\Delta v} = \frac{\Delta h}{T \Delta v}$$



Interpreting the Clapeyron Equation

- \circ Δh , Δv , and Δs are all nonzero away from the fluid critical point, and approach zero as the critical point is approached.
- o None of the coexistence curves has a zero slope.
 - Due to the non-zero value of both the entropy and enthalpy changes accompanying phase transitions.
 - \circ Due to Δv being non-zero.
- Generally, the heat of fusion and volume change on melting are positive.
 - Leads to the positive slope of the S-L curves.
 - Water is an exception to this.



Solid benzene sinks in liquid benzene (the usual), but ice floats in liquid water (at left).



Clausius-Clapeyron Equation I

- o Applies to V-L/V-S equilibria.
 - o At temperatures for which the vapor pressure is not very high. Assumes the vapor phase is ideal gas, then substitute in the Clapeyron equation

$$v^g \gg v^f \Rightarrow \Delta v \approx v^g \qquad \Delta v^{fg} \approx v^g = RT / P$$

$$\frac{dP^{\text{sat}}}{dT} = \frac{P^{\text{sat}}\Delta h^{\text{fg}}}{RT^{2}} \Rightarrow \frac{d \ln P^{\text{sat}}}{dT} = \frac{\Delta h^{\text{fg}}}{RT^{2}}$$

- o Referred to as the Clausius-Clapeyron equation.
- The latent heat of vaporization is a function of temperature. Assume it is independent of temperature over small temperature intervals

$$\ln \frac{P^{\text{sat}}(T_2)}{P^{\text{sat}}(T_1)} = -\frac{\Delta h^{\text{fg}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$



Vapor Pressure Models

Oclausius-Clapeyron

$$\ln P^{\text{vap}} = A - \frac{B}{T}$$

OAntoine

$$\ln P^{\text{vap}} = A' - \frac{B'}{T + C'}$$

oRiedel

$$\ln P^{\text{vap}} = A'' + \frac{B''}{T} + C'' \ln T + DT^6$$

OHarlecher-Braun

$$\ln P^{\text{vap}} = A''' + \frac{B'''}{T} + C''' \ln T + \frac{D'P^{\text{vap}}}{T^2}$$



Estimation of Δh^{fg} at Normal Boiling Point and at $T \neq T_n$

 \circ Trouton's rule gives a rough estimate $\frac{\Delta h_n}{RT_n} \sim 10$

oRiedel equation gives estimates to within 5% of the experimental values

 $\frac{\Delta h_n}{RT_n} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{r.}}$

oThe Watson correlation may be used to estimate the latent heat of vaporization of a liquid from knowledge of a single point

$$\frac{\Delta h_2}{\Delta h_1} = \left(\frac{1 - T_{r_2}}{1 - T_{r_1}}\right)^{0.38}$$



Pitzer's Acentric Factor: Definition

- The two parameter Corresponding States Theory (CST) fails to correlate data other than these for simple fluids.
- Development of the acentric factor (to deviate from spherical shape of simple fluids)

$$\omega = -1.0 - \log(P_r^{\text{sat}})_{T_r = 0.7}$$

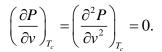
- The Acentric factor (*ω*)
 - o For simple fluids (Ar, Kr, Xe) is zero.
 - o Positive (greater than zero) for all other fluids.
 - Exception: Quantum fluids (H₂, He, Ne) which do not conform to CST unless some effective critical parameters are introduced.

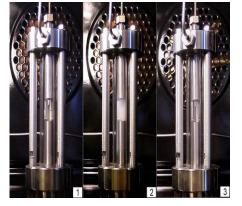


Name	Formula	<i>T</i> _c (K)	P _c (bar)	ω	$\Delta \underline{H}^{ ext{vap}}$ (kJ/mol)	$\Delta \underline{H}^{\text{fus}}$ (kJ/mol)	(cm^{3}/mol)	T (K) for <u>V</u> L
Argon	Ar	150.86	48.98	-0.002	6.43		29.10	90.00
Tetrachloromethane (carbon tetrachloride)	CCI ₄	556.3	45.57	0.194ª	29.82	3.28	97.07	298.15
Tetrafluoromethane	CF ₄	227.51	37.45	0.177			56.41	153.15
Chlorodifloromethane (R-22)	CHCIF ₂	369.28	49.86	0.221	20.22	4.12	59.08	213.15
Trichloromethane (chloroform)	CHCI ₃	536.50	55.00	0.216ª	29.24	8.80	80.68	298.15
Methane	CH ₄	190.56	45.99	0.011	8.17	0.94	35.54	90.68
Methanol	CH₃OH	512.64	80.97	0.565	35.21	3.18	40.73	298.15
Carbon monoxide	CO	132.85	34.94	0.045	6.04	0.84	34.88	81.00
Carbon dioxide	CO ₂	304.12	73.74	0.225		9.02		
Hydrogen	H ₂	33.25	12.97	-0.216	0.89	0.12	29.39	20.00
Water	H ₂ O	647.14	220.64	0.344	40.66	6.01	18.07	298.15
Nitrogen	N_2	126.2	33.98	0.037	5.58	0.72	34.84	78.00
Ammonia	NH ₃	406.6ª	112.7ª	0.252 ^a			25.0e	240e
Oxygen	O ₂	154.58	50.43	0.022 ^a	6.82	0.44	27.85	90.00



- The inflection point on the phase diagram where the liquid and vapor phases can not be distinguished from each other, because their properties are the same is called the critical point.
- The critical point is the highest pressure and highest temperature at which a pure chemical species can exist in vapor-liquid equilibrium.
- The critical condition is used to determine the parameters of some equations of state.





1. Subcritical ethane, liquid and gas phase coexist 2. Critical point (32.17 °C, 48.72 bar), opalescence 3. Supercritical ethane, fluid



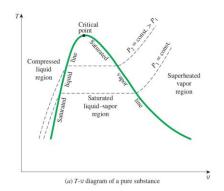
Critical Versus Triple Points

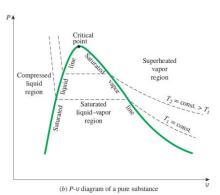
Critical Point	Triple Point
Lies at the endpoint of the phase equilibrium curve	The point where the three equilibrium curves meet
Critical temperature is usually higher than the standard/reference temperature	Temperature at the critical point is usually lower than the standard/reference temperature
Critical pressure is generally higher than standard/reference pressure	Triple point pressure is generally lower than standard/reference pressure
Only liquid and gaseous phases converge at equilibrium	All three phase: gas, liquid and solid coexist in equilibrium
Degree of freedom = 1	Degrees of freedom = 0 (invariant)



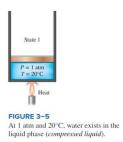
PV and TV Phase Diagrams

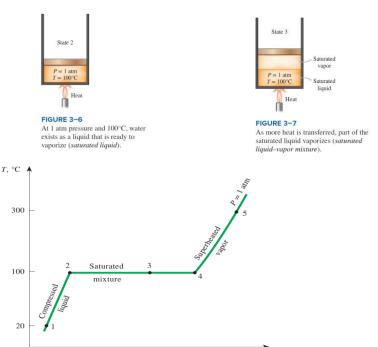
- oLiquids have steep isotherms, on a PV diagram, since liquid volume changes little with large changes in pressure.
- OVapors have smoothly varying isotherms due to the changes of vapor volume upon changes on pressure.











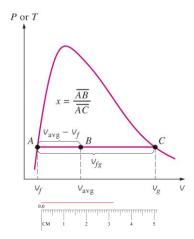


Quality

 Quality, x: The ratio of the mass of vapor to the total mass of the mixture.

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

- OQuality 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.





Quality

 \circ Quality can be calculated from any thermodynamics property θ by knowing the state point.

$$x = \frac{\theta - \theta_f}{\theta_g - \theta_f} = \frac{\theta - \theta_f}{\theta_{fg}}$$

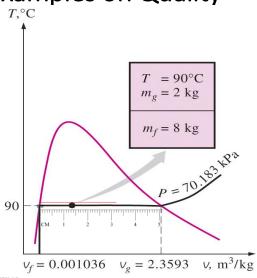
θ can be any property e.g., v, u, h, s.

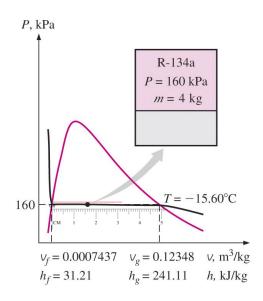
 Knowing quality enables us to find the properties of a mixture using the formula

$$\theta = x \, \theta_g + (1 - x) \theta_f = \theta_f + x \, \theta_{fg}$$



Examples on Quality







EXAMPLE 3-4 Pressure and Volume of a Saturated Mixture

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.

SOLUTION A rigid tank contains saturated mixture. The pressure and the volume of the tank are to be determined.

Analysis (a) The state of the saturated liquid–vapor mixture is shown in Fig. 3–35. Since the two phases coexist in equilibrium, we have a saturated mixture, and the pressure must be the saturation pressure at the given temperature:

$$P = P_{\text{sat } @ 90^{\circ}\text{C}} = 70.183 \text{ kPa}$$
 (Table A-4)

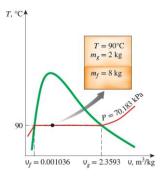
(b) At 90°C, we have v_f = 0.001036 m³/kg and v_g = 2.3593 m³/kg (Table A-4). One way of finding the volume of the tank is to determine the volume occupied by each phase and then add them:

$$V = V_f + V_g = m_f v_f + m_g v_g$$

= (8 kg)(0.001036 m³/kg) + (2 kg)(2.3593 m³/kg)
= **4.73 m**³

Another way is to first determine the quality x, then the average specific volume v, and finally the total volume:

$$x = \frac{m_g}{m_t} = \frac{2 \text{ kg}}{10 \text{ kg}} = 0.2$$



$$U = U_f + xU_{fg}$$

= 0.001036 m³/kg + (0.2)[(2.3593 - 0.001036) m³/kg]
= 0.473 m³/kg

and

$$V = mv = (10 \text{ kg})(0.473 \text{ m}^3/\text{kg}) = 4.73 \text{ m}^3$$

Discussion The first method appears to be easier in this case since the masses of each phase are given. In most cases, however, the masses of each phase are not available, and the second method becomes more convenient.



EXAMPLE 3–5 Properties of Saturated Liquid–Vapor Mixture

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.

SOLUTION A vessel is filled with refrigerant-134a. Some properties of the refrigerant are to be determined.

Analysis (a) The state of the saturated liquid–vapor mixture is shown in Fig. 3–36. At this point we do not know whether the refrigerant is in the compressed liquid, superheated vapor, or saturated mixture region. This can be determined by comparing a suitable property to the saturated liquid and saturated vapor values. From the information given, we can determine the specific volume:

$$v = \frac{V}{m} = \frac{0.080 \text{ m}^3}{4 \text{ kg}} = 0.02 \text{ m}^3/\text{kg}$$

At 160 kPa, we read

$$v_f = 0.0007435 \text{ m}^3/\text{kg}$$

 $v_o = 0.12355 \text{ m}^3/\text{kg}$ (Table A–12)

Obviously, $v_f < v < v_g$, and the refrigerant is in the saturated mixture region. Thus, the temperature must be the saturation temperature at the specified pressure:

$$T = T_{\text{sat @ 160 kPa}} = -15.60^{\circ}\text{C}$$

(b) Quality can be determined from

$$x = \frac{v - v_f}{v_{fg}} = \frac{0.02 - 0.0007435}{0.12355 - 0.0007435} = \mathbf{0.157}$$

(c) At 160 kPa, we also read from Table A–12 that $h_{\!f}=31.18$ kJ/kg and $h_{\!f\!g}=209.96$ kJ/kg. Then,

$$h = h_f + xh_{fg}$$

= 31.18 kJ/kg + (0.157)(209.96 kJ/kg)
= **64.1 kJ/kg**

(d) The mass of the vapor is

$$m_o = xm_t = (0.157)(4 \text{ kg}) = 0.628 \text{ kg}$$

and the volume occupied by the vapor phase is

$$V_g = m_g U_g = (0.628 \text{ kg})(0.12355 \text{ m}^3/\text{kg}) = 0.0776 \text{ m}^3 \text{ (or 77.6 L)}$$

The rest of the volume (2.4 L) is occupied by the liquid.



Reference State and Reference Values

- o 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.
- o The reference state for:
 - o water is the saturated liquid at its triple point (0.01°C and 0.6117 kPa)
 - R-134a is saturated liquid at -40°C.
- o 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.



		Temperature table Specific volume, m³/kg		Internal energy, kJ/kg		Enthalpy, kJ/kg			<i>Entropy,</i> kJ/kg∙K			
Temp.,	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,	Evap., s_{fg}	Sat. vapor, s_g
0.01 5 10 15 20	0.6117 0.8725 1.2281 1.7057 2.3392	0.001000 0.001000 0.001000 0.001001 0.001002	206.00 147.03 106.32 77.885 57.762	0.000 21.019 42.020 62.980 83.913	2360.8 2346.6	2374.9 2381.8 2388.7 2395.5 2402.3	0.001 21.020 42.022 62.982 83.915	2500.9 2489.1 2477.2 2465.4 2453.5	2500.9 2510.1 2519.2 2528.3 2537.4	0.0000 0.0763 0.1511 0.2245 0.2965	9.1556 8.9487 8.7488 8.5559 8.3696	9.1556 9.0249 8.8999 8.7803 8.6661
25 30		0.001003	43.340 32.879	104.83 125.73	2304.3	2409.1 2415.9	104.83 125.74	2441.7 2429.8	2546.5 2555.6	0.3672 0.4368	8.1895 8.0152	8.5567 8.4520
TABL	E A-11											
Saturat	ed refrigera	nt-134a—T	emperature	able								
		Specific	volume,	Inte	ernal ener	зу,		Enthalpy kJ/kg	,		Entropy, kJ/kg·K	
		m ³	/kg		kJ/kg			KJ/Kg			KJ/Kg IX	
Temp., $T ^{\circ}$ C	Sat. press., P _{sat} kPa	Sat. liquid, V_f	Sat. vapor, U _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
	press.,	Sat. liquid,	Sat. vapor, v _g 3 0.36064 2 0.32718 0.29740	liquid,	Evap.,	vapor,	liquid,	Evap.,	vapor,	liquid,	Evap.,	vapor

EXAMPLE 3-9 The Use of Steam Tables to Determine Properties

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

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

SOLUTION Properties and phase descriptions of water are to be determined at various states.

Analysis (a) The quality is given to be x = 0.6, which implies that 60 percent of the mass is in the vapor phase and the remaining 40 percent is in the liquid phase. Therefore, we have saturated liquid–vapor mixture at a pressure of 200 kPa. Then the temperature must be the saturation temperature at the given pressure:

$$T = T_{\text{sat @ 200 kPa}} = 120.21^{\circ}\text{C}$$
 (Table A-5)

At 200 kPa, we also read from Table A–5 that u_f = 504.50 kJ/kg and u_{fg} = 2024.6 kJ/kg. Then the average internal energy of the mixture is

$$u = u_f + x u_{fg}$$

= 504.50 kJ/kg + (0.6)(2024.6 kJ/kg)
= 1719.26 kJ/kg

(b) This time the temperature and the internal energy are given, but we do not know which table to use to determine the missing properties because we have no clue as to whether we have saturated mixture, compressed liquid, or superheated vapor. To determine the region we are in, we first go to the saturation table (Table A-4) and determine the u_f and u_g values at the given temperature. At 125°C, we read $u_f = 524.83 \, \mathrm{kJ/kg}$ and $u_g = 2534.3 \, \mathrm{kJ/kg}$. Next we compare the given u value to these u_f and u_g values, keeping in mind that

$$\begin{array}{ll} \text{if} & u < u_f & \text{we have } compressed \ liquid \\ \text{if} & u_f \leq u \leq u_g & \text{we have } saturated \ mixture \\ \text{if} & u > u_g & \text{we have } superheated \ vapor \end{array}$$



In our case the given u value is 1600 kJ/kg, which falls between the u_f and u_g values at 125°C. Therefore, we have saturated liquid-vapor mixture. Then the pressure must be the saturation pressure at the given temperature:

$$P = P_{\text{sat } \oplus 125^{\circ}\text{C}} = 232.23 \text{ kPa}$$
 (Table A-4)

The quality is determined from

$$x = \frac{u - u_f}{u_{fo}} = \frac{1600 - 524.83}{2009.5} = 0.535$$

The preceding criteria for determining whether we have compressed liquid, saturated mixture, or superheated vapor can also be used when enthalpy h or specific volume v is given instead of internal energy u, or when pressure is given instead of temperature.

(c) This is similar to case (b), except pressure is given instead of temperature. Following the argument given above, we read the u_f and u_g values at the specified pressure. At 1 MPa, we have $u_f = 761.39 \, \text{kJ/kg}$ and $u_g = 2582.8 \, \text{kJ/kg}$. The specified u value is 2950 kJ/kg, which is greater than the u_g value at 1 MPa. Therefore, we have superheated vapor, and the temperature at this state is determined from the superheated vapor table by interpolation to be

$$T = 395.2$$
°C (Table A–6)

We would leave the quality column blank in this case since quality has no meaning for a superheated vapor. (d) In this case the temperature and pressure are given, but again we cannot tell which table to use to determine the missing properties because we do not know whether we have saturated mixture, compressed liquid, or superheated vapor. To determine the region we are in, we go to the saturation table (Table A–5) and determine the saturation temperature value at the given pressure. At 500 kPa, we have $T_{\rm sat}=151.83\,^{\circ}\mathrm{C}$. We then compare the given T value to this $T_{\rm sat}$ value, keeping in mind that

if
$$T < T_{\text{sat @ given }P}$$
 we have compressed liquid
if $T = T_{\text{sat @ given }P}$ we have saturated mixture
if $T > T_{\text{sat @ given }P}$ we have superheated vapor

In our case, the given T value is 75°C, which is less than the $T_{\rm sat}$ value at the specified pressure. Therefore, we have compressed liquid (Fig. 3–42), and normally we would determine the internal energy value from the compressed liquid table. But in this case the given pressure is much lower than the lowest pressure value in the compressed liquid table (which is 5 MPa), and therefore we are justified to treat the compressed liquid as saturated liquid at the given temperature (not pressure):

$$u \cong u_{f@75^{\circ}C} = 313.99 \text{ kJ/kg}$$
 (Table A-4)

We would leave the quality column blank in this case since quality has no meaning in the compressed liquid region.

(e) The quality is given to be x = 0, and thus we have saturated liquid at the specified pressure of 850 kPa. Then the temperature must be the saturation temperature at the given pressure, and the internal energy must have the saturated liquid value:

$$T = T_{\text{sat } \oplus 850 \text{ kPa}} = 172.94^{\circ}\text{C}$$

 $u = u_{f \oplus 850 \text{ kPa}} = 731.00 \text{ kJ/kg}$ (Table A–5)

