

PROPERTIES OF PURE SUBSTANCES

SUMMARY

PURE SUBSTANCE

- **Pure substance**: A substance that has a fixed chemical composition throughout.
- Compressed liquid (sub-cooled liquid): A substance that it is not about to vaporize.
- <u>Saturated liquid</u>: A liquid that is about to vaporize.
- **<u>Saturated vapor</u>**: A vapor that is *about to condense*.
- <u>Saturated liquid–vapor mixture</u>: 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).



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.

- 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 (Enthalpy): 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.

PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

property diagrams such as the T-v, P-v, and P-T diagrams for pure substances.



T-v diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).



T-v diagram of a pure substance.



no distinct phase-change (boiling) process.

Critical point: The point at which the saturated liquid and saturated vapor states are identical.



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.

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

VAPOR

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



P-T diagram of pure substances.

Saturated Liquid and Saturated Vapor States

- **<u>Table A-4</u>**: Saturation properties of water under temperature.
- **<u>Table A-5</u>**: Saturation properties of water under pressure.

A partial list of Table A-4.

	Sat.		Specific volume			
			m ³ /kg			
Temp.	press.		Sat.		Sat.	
°C	kPa		liquid		vapor	
Т	P _{sat}		V_{f}		V_g	
85	57.868		0.001032		2.8261	
90	70.183		0.001036		2.3593	
95	84.609		0.0010)40	1.980)8
•	-	a.	•			
Specific temperature		Specific volume of saturated liquid				
Corresponding					Specific	
sat	urati	on			volume of	
pre	essure	e	saturate		irated	
					vapor	

 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.

Liquid – Vapour Mixture



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)

Compressed Liquid

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

 $y \cong y_{f @ T}$

 $y \rightarrow v, u, \text{ or } h$

A more accurate relation for h

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

Given: P and T $V \cong V_{f @ T}$ $u \cong u_{f @ T}$ $h \cong h_{f @ T}$

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

Compressed liquid is characterized by

Higher pressures $(P > P_{sat} \text{ at a given } T)$ Lower tempreatures $(T < T_{sat} \text{ at a given } P)$ Lower specific volumes $(v < v_f \text{ at a given } P \text{ or } T)$ Lower internal energies $(u < u_f \text{ at a given } P \text{ or } T)$ Lower enthalpies $(h < h_f \text{ at a given } P \text{ or } T)$

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.

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

Pv = RT Ideal gas equation of state

COMPRESSIBILITY FACTOR—A MEASURE OF DEVIATION FROM IDEAL-GAS BEHAVIOR

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

$$Pv = ZRT$$
$$Z = \frac{Pv}{RT}$$
$$Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}$$

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).

<u>COMPRESSIBILITY FACTOR—A MEASURE</u> OF DEVIATION FROM IDEAL-GAS BEHAVIOR

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.



The compressibility factor is unity for ideal gases.



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

Reduced pressure



Reduced temperature



Pseudo-reduced specific volume



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

$$P_{R} = \frac{P}{P_{cr}}$$

$$V_{R} = \frac{V}{RT_{cr}/P_{cr}}$$

$$Z = \dots$$
(Fig. A-15)



Comparison of Z factors for various gases.



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

OTHER EQUATIONS OF STATE

Van der Waals Equation of State

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

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

This model includes two effects not considered in the idealgas 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.

OTHER EQUATIONS OF STATE

Beattie-Bridgeman Equation of State

$$P = \frac{R_u T}{\overline{\nu}^2} \left(1 - \frac{c}{\overline{\nu} T^3} \right) (\overline{\nu} + B) - \frac{A}{\overline{\nu}^2}$$
$$A = A_0 \left(1 - \frac{a}{\overline{\nu}} \right) \quad B = B_0 \left(1 - \frac{b}{\overline{\nu}} \right)$$

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

OTHER EQUATIONS OF STATE

Benedict-Webb-Rubin Equation of State

$$P = \frac{R_u T}{\overline{\nu}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2} \right) \frac{1}{\overline{\nu}^2} + \frac{b R_u T - a}{\overline{\nu}^3} + \frac{a \alpha}{\overline{\nu}^6} + \frac{c}{\overline{\nu}^3 T^2} \left(1 + \frac{\gamma}{\overline{\nu}^2} \right) e^{-\gamma/\overline{\nu}^2}$$

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

Virial Equation of State

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

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



Percentage of error involved in various equations of state for nitrogen (% error = $[(|v_{table} - v_{equation}|)/v_{table}] \times 100$).

THE END

THANK YOU