where a system may exist in more than one phase that satisfies the criteria for stability, the system adopts the *most stable* phase, rendering the other phases *metastable*. When two phases are equally stable we obtain the saturation point, namely, a state where two (or more) phases exist in equilibrium with each other. We may identify the stable and metastable phases by comparing their fugacity. Suppose we follow the ϕ isotherm starting from point D. Initially, the compressibility equation has a single root and the only possible phase is the vapor. Beginning with some pressure, the compressibility equation has three real roots, indicating that a liquid phase is possible. However, the fugacity coefficient of this liquid is higher than that of the vapor: the liquid phase is *metastable*, meaning less stable than the vapor at the same pressure and temperature. A metastable phase may materialize briefly, but thermal fluctuations will eventually cause the system to revert to the more stable phase. At saturation, both phases have the same fugacity coefficient. Past this point, the situation is reversed: the liquid phase is more stable than the vapor because its fugacity coefficient is lower. In all cases the most stable phase is the one with the lower fugacity coefficient. This also means that the more stable phase has lower Gibbs energy, lower residual Gibbs energy and lower fugacity, compared to the metastable phase.[3]

7.6   Phase Diagrams from Equations of State

At this point we have reached one of the main goals we set out to achieve: obtain the properties of a pure fluid at any temperature and pressure. The two pieces of information that make this calculation possible are the equation of state and the ideal-gas heat capacity as a function of temperature. The equation of state allows the calculation of all residual properties and the determination of the phase boundary, namely of the saturation pressure and the properties of the saturated phases. Thus we have the tools to compute the entire phase diagram of the pure fluid. This calculation is demonstrated with the example below.

Example 7.10: Phase Diagram of Ethylene
Calculate the phase diagram of ethylene using the SRK equation. The reference state is saturated liquid at 110 K.

Solution   We will demonstrate the calculation by obtaining all properties along an isotherm, from the compressed liquid region to the superheated vapor. The calculation can then repeated with other temperatures to obtain the complete phase diagram. We pick $T = 260$ K.

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3. To reach this conclusion we write $G = G^{\text{ig}} + G^{R}$. Since both phases are the same pressure and temperature, the term G^{ig} is common in both phases. Then, the phase with the lower fugacity coefficient has the lower residual Gibbs free energy and also the lower molar Gibbs free energy.

Saturation pressure From Figure 7-3 we see that the saturation pressure at 260 K must be between the pressures of points B (~ 15 bar) and C (~ 35 bar). Using $P = 29$ bar as the trial pressure, we find the following roots for the compressibility factor:

$$Z_1 = 0.1104, \quad Z_2 = 0.2244, \quad Z_3 = 0.6651.$$

Using $Z_L = Z_1$ in eq. (7.21) we find $\phi_L = 0.7733$; with $Z_V = Z_3$ the same equation gives $\phi_V = 0.7539$. These values are not sufficiently close. Therefore we repeat the calculation with different pressures in small increments and construct the table below:

P (bar)	Z_L	Z_V	ϕ_L	ϕ_V	ϕ_L/ϕ_V
29	0.1104	0.6651	0.7733	0.7539	1.0256
30	0.1136	0.6461	0.7503	0.7452	1.0069
31	0.1169	0.6255	0.7289	0.7363	0.9898
32	0.1201	0.6026	0.7088	0.7274	0.9744

The saturation pressure is between ~~31~~ 30 and ~~32~~ 31 bar. By refining the pressure step (or by simple interpolation between the values in the table), we find

$$P^{\text{sat}} = 30.39 \text{ bar}.$$

The value reported in Perry's *Handbook* is 30.046 bar.

Properties. The enthalpy and entropy are calculated using eqs. (5.62) and (5.64):

$$H = \Delta H_{\text{ref}}^{\text{ig}} + H^R - H_0^R + H_0, \quad\quad\quad [5.62]$$

$$S = \Delta S_{\text{ref}}^{\text{ig}} + S^R - S_0^R + S_0, \quad\quad\quad [5.64]$$

with $H_0 = 0$, $S_0 = 0$. Since the reference state is the saturated liquid at $T_0 = 110$ K, we must first calculate the saturation pressure at this temperature. The calculation is done as in the previous step. We find,

$$P_0 = 0.00333 \text{ bar}, \quad H_0^R = -15565.8 \text{ J/mol}, \quad S_0^R = -141.505 \text{ J/mol K}$$

For subcritical isotherms the procedure for the calculation of the enthalpy and entropy is as follows:

1. Fix temperature.

2. Calculate the saturation pressure.

3. Fix pressure.

4. Determine the phase of the system at the given pressure: if $P < P^{\text{sat}}$, the phase is vapor; if $P > P^{\text{sat}}$ the phase is compressed liquid; if $P = P^{\text{sat}}$, the system is saturated.

5. Solve for the compressibility factor. If three real roots, pick according to the phase.

6. Calculate the residual properties as usual.

7. Calculate the ideal-gas parts of enthalpy and entropy.

8. Combine the ideal gas and residual parts to obtain the absolute properties.

9. Change the pressure and return to step 4 to repeat the calculation.

The calculation for supercritical isotherms is simpler. In this case there is no saturation pressure and the compressibility equation has one real root only. Therefore, steps 2 and 4 are skipped, otherwise the calculation is identical.

The table below shows results at three pressures, 40 bar (compressed liquid), 30.3929 bar (saturated vapor-liquid) and 20 bar (superheated vapor).

	Phase			
	Comp. liq.	Sat. liq.	Sat. vap.	S/H vap.
T (K)	260	260	260	260
P (bar)	40	30.3929	30.3929	20
Z	0.145477	0.114908	0.63825	0.797499
H (J/mol)	11056.1	11238.9	18428.9	19528.4
S (J/mol K)	60.04	61.04	88.70	95.46

Other properties may be computed from their relationship to the properties shown here. For example, the internal energy is calculated as $U = U - ZRT$, the Gibbs free energy as $G = H - TS$, and so on.

Figure 7-5 shows the pressure-enthalpy diagram of ethylene calculated by this method. The graph shows the phase boundary and representative isotherms.

7.7   Summary

In this chapter we developed the theoretical tools for the study of saturated phases, namely, phases that coexist in equilibrium with each other. The fundamental property is the Gibbs free energy, which has the same value in both phases. This fundamental equality is the basis of all the results obtained in this chapter. Fugacity and the fugacity coefficient are auxiliary variables introduced for convenience. They are both related to the Gibbs free energy but are more convenient to work with because they do not require a reference state. In addition, they reduce to very simple expressions in the ideal-gas state.

An important conclusion in this chapter is that all properties of a pure fluid at saturation can be calculated from the equation of state. The equation of state,