

CHAPTER II

HIGH-PRESSURE VAPOR-LIQUID EQUILIBRIA

2.1 THERMODYNAMICS OF PHASE EQUILIBRIA [8]

The fundamental equations of phase equilibrium are commonly written in terms of chemical potentials, but for practical engineering work it is useful to rewrite them in terms of fugacities. A vapor phase and a liquid phase are in thermodynamic equilibrium when both are at the same temperature and when f_i , the fugacity of any component i in the vapor phase, is equal to that in the liquid phase :

$$f_i^V = f_i^L \quad (2.1)$$

where superscript V stands for vapor and superscript L stands for liquid. Neglecting gravitational effects, semipermeable barriers, etc., we assume that the total pressure P is the same in both phases.

Equation (2.1) is of little practical use unless the fugacity of each component can be related to the experimentally accessible quantities: temperature, pressure and compositions. To facilitate the desired relations, we require the auxiliary functions, the fugacity coefficient ϕ_i .



2.1.1 Fugacity Coefficient

In the vapor phase, the fugacity coefficient is defined as the ratio of fugacity to partial pressure as

$$\phi_i^V = \frac{f_i^V}{y_i P} \quad (2.2)$$

and is always equal to 1 as $P \rightarrow 0$, which is represented for ideal gas by

$$\lim_{P \rightarrow 0} \left(\frac{f_i^V}{y_i P} \right) = 1 \quad (2.3)$$

where y_i denotes vapor mole fraction of component i

A similar definition for ϕ_i^L could be used for the liquid phase.

$$\phi_i^L = \frac{f_i^L}{x_i P} \quad (2.4)$$

The fugacity coefficient is a function of pressure, temperature and composition; it is related to the volumetric properties of the mixture by the thermodynamic relation [7]

$$\ln \phi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j} - \frac{RT}{V} \right] dV - \ln Z \quad (2.5)$$

where n_i stands for the number of moles of component i , Z is the compressibility factor ($Z = Pv/RT$) at T and P .

Equation (2.5) can be used to calculate fugacity coefficients of a component in both vapor and liquid phases at equilibrium by integration of volumetric data (PVT data) which is preferably in the form of an equation of state.

To obtain a numerical result from Equation (2.5), we require a pressure-explicit equation of state which holds for a mixture of interest in both the vapor phase and the liquid phase, the derivative of P with respect to n_i must be found and then integrate Equation (2.5)

2.2 PHASE BEHAVIOR OF NATURAL GAS AT HIGH PRESSURE [9]

The pressure-volume-temperature (PVT) behavior of hydrocarbon systems is a complex and difficult subject. The PVT interrelations are usually presented graphically and show the amount of liquid and vapor present for various combinations of temperature and pressure. A pressure-temperature diagram for a typical natural gas is shown in Figure 2.1

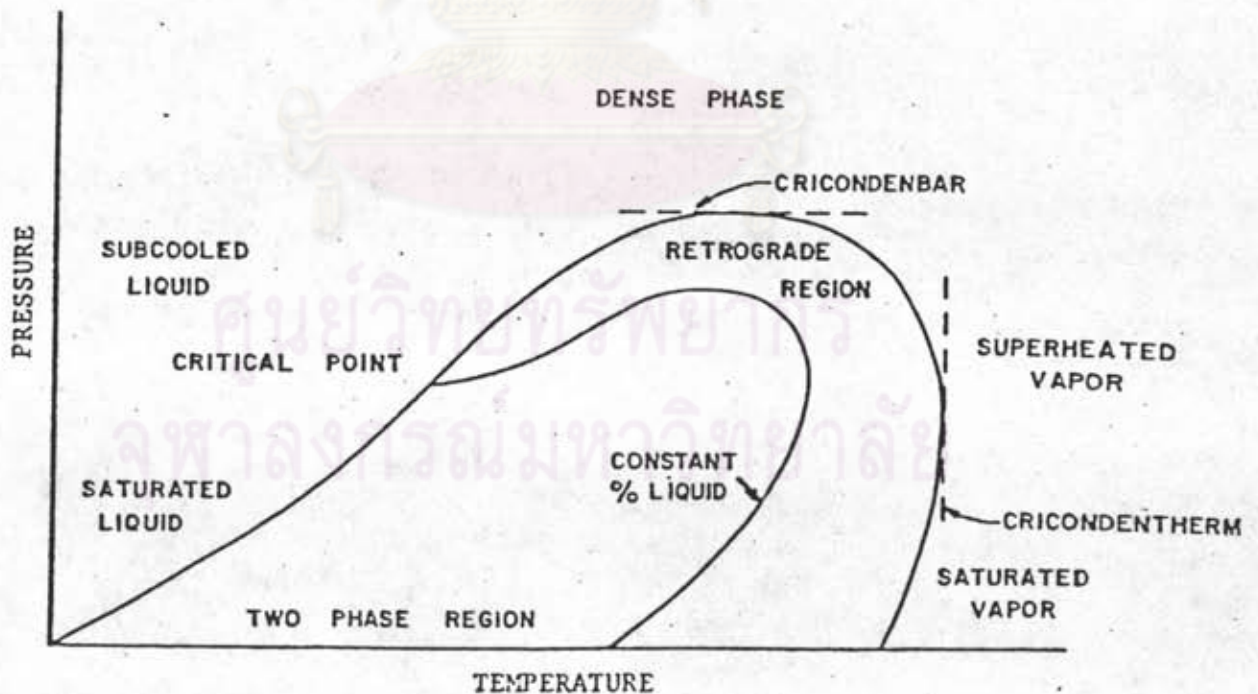


figure 2.1 Phase Envelope for a Typical Natural Gas Mixture.

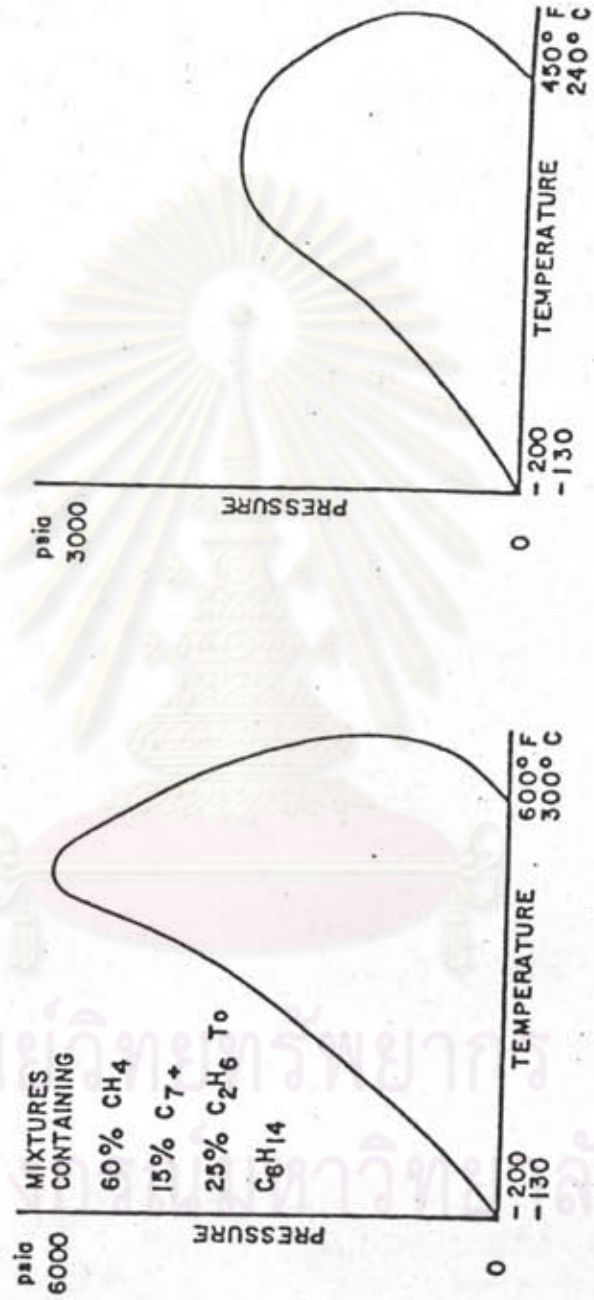


figure 2.2 Typical Pressure-Temperature Envelopes for Reservoir Fluids.

Significant effects on the shape of the pressure-temperature envelope can be observed for concentrations and types of molecular species present in mixtures. Some envelopes for typical reservoir fluids are shown in Figure 2.2. The location of the critical point along the pressure temperature envelope is a function of the molecular species present and the relative concentration of the individual species. Figure 2.3 shows the potential range of critical point locations along the pressure temperature envelope. The theoretical possible range for the critical is from point A to point D. The practical possible range is from point A to point C for naturally occurring mixtures. Relative lean natural gas reservoir systems (mole percent methane greater than about 80%) and typical natural gas process streams will have critical points located between point A and

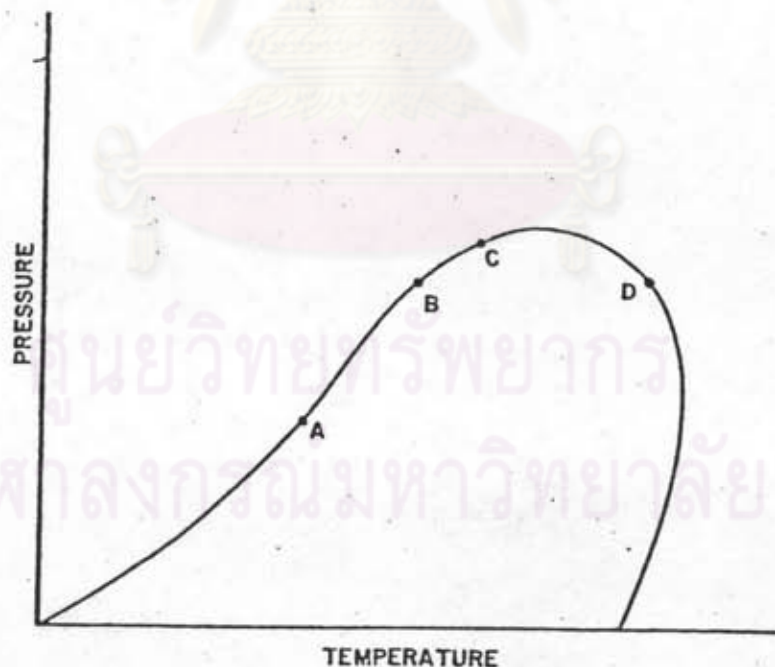


figure 2.3 Possible Critical Point Locations Along the Pressure-Temperature Envelope.

B. As the reservoir fluid becomes richer (i.e. contains more propane, butane, pentane, and condensate or crude oil) the critical point will shift from point A toward point B or C. Point C probably would be representative of most crude oil reservoir fluids.

One of the most poorly understood phenomenon in vapor-liquid phase behavior at high pressure is that of retrograde condensation and/or retrograde vaporization, "Retrograde" simply means backwards, or the reverse of normal. Retrograde behavior in a multicomponent system comes about because of the location of the true critical point for the mixture and the manner in which the bubble point and dew point lines are separated from each other. A typical multicomponent system phase envelope with retrograde region is show in Figure 2.4. The retrograde region in Figure 2.4 is that section of the pressure temperature diagram which falls to the right of the true critical point for the mixture. Increasing the temperature at constant pressure may cause liquid to condense. Increasing the pressure at constant temperature may cause liquid to vaporize. This cannot happen for pure component.

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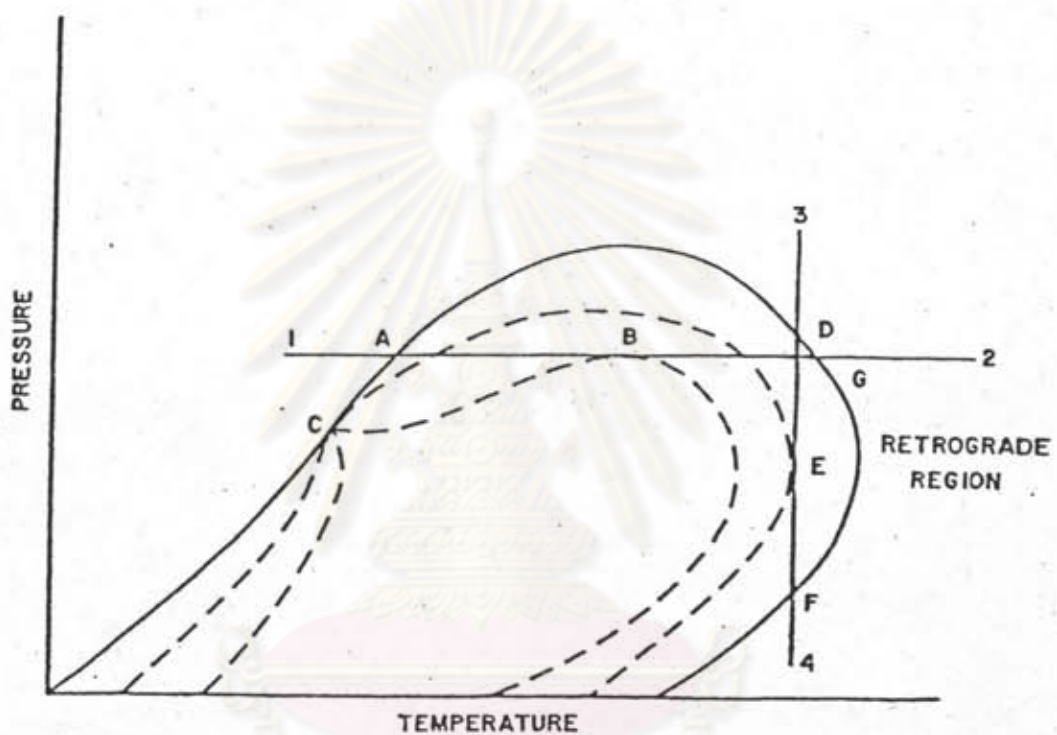


figure 2.4 Retrograde Behavior.

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