1

Fundamentals of Hydrocarbon Phase Behavior

A *PHASE* IS DEFINED AS ANY homogeneous part of a system that is physically distinct and separated from other parts of the system by definite boundaries. For example, ice, liquid water, and water vapor constitute three separate phases of the pure substance H_2O, because each is homogeneous and physically distinct from the others; moreover, each is clearly defined by the boundaries existing between them. Whether a substance exists in a solid, liquid, or gas phase is determined by the temperature and pressure acting on the substance. It is known that ice (solid phase) can be changed to water (liquid phase) by increasing its temperature and, by further increasing the temperature, water changes to steam (vapor phase). This change in phases is termed *phase behavior*.

Hydrocarbon systems found in petroleum reservoirs are known to display multiphase behavior over wide ranges of pressures and temperatures. The most important phases that occur in petroleum reservoirs are a liquid phase, such as crude oils or condensates, and a gas phase, such as natural gases.

The conditions under which these phases exist are a matter of considerable practical importance. The experimental or the mathematical determinations of these conditions are conveniently expressed in different types of diagrams, commonly called *phase diagrams*.

The objective of this chapter is to review the basic principles of hydrocarbon phase behavior and illustrate the use of phase diagrams in describing and characterizing the volumetric behavior of single-component, two-component, and multicomponent systems.

Single-Component Systems

The simplest type of hydrocarbon system to consider is that containing one component. The word *component* refers to the number of molecular or atomic species present in the substance.

A single-component system is composed entirely of one kind of atom or molecule. We often use the word *pure* to describe a single-component system.

The qualitative understanding of the relationship between temperature T, pressure p, and volume V of pure components can provide an excellent basis for understanding the phase behavior of complex petroleum mixtures. This relationship is conveniently introduced in terms of experimental measurements conducted on a pure component as the component is subjected to changes in pressure and volume at a constant temperature. The effects of making these changes on the behavior of pure components are discussed next.

Suppose a fixed quantity of a pure component is placed in a cylinder fitted with a frictionless piston at a fixed temperature T_1. Furthermore, consider the initial pressure exerted on the system to be low enough that the entire system is in the vapor state. This initial condition is represented by point E on the pressure/volume phase diagram (p-V diagram) as shown in Figure 1–1. Consider the following sequential experimental steps taking place on the pure component:

1. The pressure is increased isothermally by forcing the piston into the cylinder. Consequently, the gas volume decreases until it reaches point F on the diagram, where the liquid begins to condense. The corresponding pressure is known as the *dew-point pressure*, p_d, and defined as the pressure at which the first droplet of liquid is formed.
2. The piston is moved further into the cylinder as more liquid condenses. This condensation process is characterized by a constant pressure and represented by the horizontal line FG. At point G, traces of gas remain and the corresponding pressure is called the *bubble-point pressure*, p_b, and defined as the pressure at which the first sign of

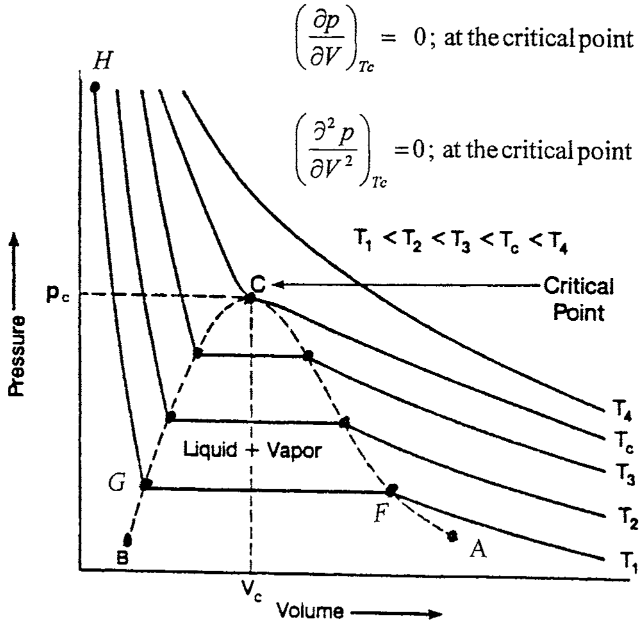


FIGURE 1–1 *Typical pressure/volume diagram for a pure component.*

gas formation is detected. A characteristic of a single-component system is that, at a given temperature, the dew-point pressure and the bubble-point pressure are equal.

3. As the piston is forced slightly into the cylinder, a sharp increase in the pressure (point H) is noted without an appreciable decrease in the liquid volume. That behavior evidently reflects the low compressibility of the liquid phase.

By repeating these steps at progressively increasing temperatures, a family of curves of equal temperatures (isotherms) is constructed as shown in Figure 1–1. The dashed curve connecting the dew points, called the *dew-point curve* (line *FC*), represents the states of the "saturated gas." The dashed curve connecting the bubble points, called the *bubble-point curve* (line *GC*), similarly represents the "saturated liquid." These two curves meet a point *C*, which is known as the *critical point*. The corresponding pressure and volume are called the *critical pressure*, p_c, and *critical volume*, V_c, respectively. Note that, as the temperature increases, the length of the straight line portion of the isotherm decreases until it eventually vanishes and the isotherm merely has a horizontal tangent and inflection point at the critical point. This isotherm temperature is called the *critical temperature*, T_c, of that single component. This observation can be expressed mathematically by the following relationship:

$$\left(\frac{\partial p}{\partial V}\right)_{T_c} = 0, \text{ at the critical point} \tag{1–1}$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c} = 0, \text{ at the critical point} \tag{1–2}$$

Referring to Figure 1–1, the area enclosed by the area *AFCGB* is called the *two-phase region* or the *phase envelope*. Within this defined region, vapor and liquid can coexist in equilibrium. Outside the phase envelope, only one phase can exist.

The critical point (point *C*) describes the critical state of the pure component and represents the limiting state for the existence of two phases, that is, liquid and gas. In other words, for a single-component system, the critical point is defined as the highest value of pressure and temperature at which two phases can coexist. A more generalized definition of the critical point, which is applicable to a single- or multicomponent system, is this: The critical point is the point at which all intensive properties of the gas and liquid phases are equal.

An intensive property is one that has the same value for any part of a homogeneous system as it does for the whole system, that is, a property independent of the quantity of the system. Pressure, temperature, density, composition, and viscosity are examples of intensive properties.

Many characteristic properties of pure substances have been measured and compiled over the years. These properties provide vital information for calculating the thermodynamic properties of pure components as well as their mixtures. The most important of these properties include

- Critical pressure, p_c.
- Critical temperature, T_c.
- Critical volume, V_c.

- Critical compressibility factor, Z_c.
- Boiling point temperature, T_b.
- Acentric factor, ω.
- Molecular weight, M.
- Specific gravity, γ.

Those physical properties needed for hydrocarbon phase behavior calculations are presented in Table 1–1 for a number of hydrocarbon and nonhydrocarbon components.

Another means of presenting the results of this experiment is shown in Figure 1–2, in which the pressure and temperature of the system are the independent parameters. Figure 1–2 shows a typical pressure/temperature diagram (p/T diagram) of a single-component system with solids lines that clearly represent three different phase boundaries: vapor-liquid, vapor-solid, and liquid-solid phase separation boundaries. As shown in the illustration, line AC terminates at the critical point (point C) and can be thought of as the dividing line between the areas where liquid and vapor exist. The curve is commonly called the *vapor-pressure curve* or the *boiling-point curve*. The corresponding pressure at any point on the curve is called the *vapor pressure*, p_v, with a corresponding temperature termed the *boiling-point temperature*.

The vapor-pressure curve represents the conditions of pressure and temperature at which two phases, vapor and liquid, can coexist in equilibrium. Systems represented by a point located below the vapor-pressure curve are composed only of the vapor phase. Similarly, points above the curve represent systems that exist in the liquid phase. These remarks can be conveniently summarized by the following expressions:

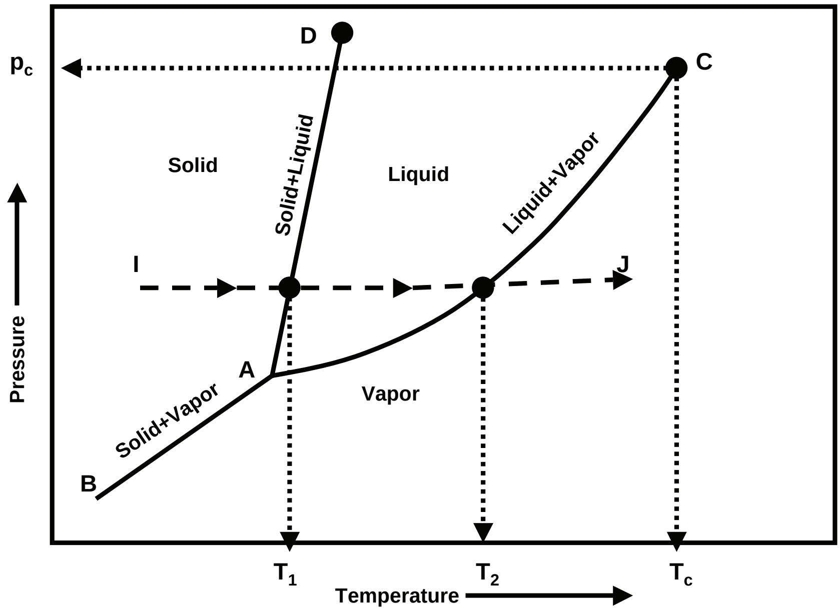


FIGURE 1–2 *Typical pressure/temperature diagram for a single-component system.*

If $p < p_v$ → the system is entirely in the vapor phase;

If $p > p_v$ → the system is entirely in the liquid phase;

If $p = p_v$ → the vapor and liquid coexist in equilibrium;

where p is the pressure exerted on the pure substance. It should be pointed out that these expressions are valid only if the system temperature is below the critical temperature T_c of the substance.

The lower end of the vapor-pressure line is limited by the triple point *A*. This point represents the pressure and temperature at which solid, liquid, and vapor coexist under equilibrium conditions. The line *AB* is called the *sublimation pressure curve* of the solid phase, and it divides the area where solid exists from the area where vapor exists. Points above *AB* represent solid systems, and those below *AB* represent vapor systems. The line *AD* is called the *melting curve* or *fusion curve* and represents the change of melting point temperature with pressure. The fusion (melting) curve divides the solid phase area from the liquid phase area, with a corresponding temperature at any point on the curve termed the *fusion* or *melting-point temperature*. Note that the solid-liquid curve (fusion curve) has a steep slope, which indicates that the triple-point for most fluids is close to their normal melting-point temperatures. For pure hydrocarbons, the melting point generally increases with pressure so the slope of the line *AD* is positive. Water is the exception in that its melting point decreases with pressure, so in this case, the slope of the line *AD* is negative.

Each pure hydrocarbon has a *p/T* diagram similar to the one shown in Figure 1–2. Each pure component is characterized by its own vapor pressures, sublimation pressures, and critical values, which are different for each substance, but the general characteristics are similar. If such a diagram is available for a given substance, it is obvious that it could be used to predict the behavior of the substance as the temperature and pressure are changed. For example, in Figure 1–2, a pure component system is initially at a pressure and temperature represented by the point *I*, which indicates that the system exists in the solid phase state. As the system is heated at a constant pressure until point *J* is reached, no phase changes occur under this isobaric temperature increase and the phase remains in the solid state until the temperature reaches T_1. At this temperature, which is identified as the melting point at this constant pressure, liquid begins to form and the temperature remains constant until all the solid has disappeared. As the temperature is further increased, the system remains in the liquid state until the temperature T_2 is reached. At T_2 (which is the boiling point at this pressure), vapor forms and again the temperature remains constant until all the liquid has vaporized. The temperature of this vapor system now can be increased until the point *J* is reached. It should be emphasized that, in the process just described, only the phase changes were considered. For example, in going from just above T_1 to just below T_2, it was stated that only liquid was present and no phase change occurred. Obviously, the intensive properties of the liquid are changed as the temperature is increased. For example, the increase in temperature causes an increase in volume with a resulting decrease in the density. Similarly, other physical properties of the liquid are altered, but the properties of the system are those of a liquid and no other phases appear during this part of the isobaric temperature increase.

TABLE 1–1 *Physical Properties for Pure Components, Physical Constants*

Physical Constants

	See Note No. ->		A.	B.		C.	D.				
								Critical constants			
Number	Compound	Formula	Molar mass (molecular weight)	Boiling point, °F 14.696 psia	Vapor pressure, psia 100 °F	Freezing point, °F 14.696 psia	Refractive index, n_D 60°F	Pressure, psia	Temperature, °F	Volume, ft^3/lbm	Number
1	Methane	CH_4	16.043	−258.73	(5000)*	−296.44*	1.00042*	666.4	−116.67	0.0988	1
2	Ethane	C_2H_6	30.070	−127.49	(800)*	−297.04*	1.20971*	706.5	89.92	0.0783	2
3	Propane	C_3H_8	44.097	−43.75	188.64	−305.73*	1.29480*	616.0	206.06	0.0727	3
4	Isobutane	C_4H_{10}	58.123	10.78	72.581	−255.28	1.3245*	527.9	274.46	0.0714	4
5	n–Butane	C_4H_{10}	58.123	31.08	51.706	−217.05	1.33588*	550.6	305.62	0.0703	5
6	Isopentane	C_5H_{12}	72.150	82.12	20.445	−255.82	1.35631	490.4	369.10	0.0679	6
7	n–Pentane	C_5H_{12}	72.150	96.92	15.574	−201.51	1.35992	488.6	385.8	0.0675	7
8	Neopentane	C_5H_{12}	72.150	49.10	36.69	2.17	1.342*	464.0	321.13	0.0673	8
9	n–Hexane	C_6H_{14}	86.177	155.72	4.9597	−139.58	1.37708	436.9	453.6	0.0688	9
10	2–Methylpentane	C_6H_{14}	86.177	140.47	6.769	−244.62	1.37387	436.6	435.83	0.0682	10
11	3–Methylpentane	C_6H_{14}	86.177	145.89	6.103	———	1.37888	453.1	448.4	0.0682	11
12	Neohexane	C_6H_{14}	86.177	121.52	9.859	−147.72	1.37126	446.8	420.13	0.0667	12
13	2,3–Dimethylbutane	C_6H_{14}	86.177	136.36	7.406	−199.38	1.37730	453.5	440.29	0.0665	13
14	n–Heptane	C_7H_{16}	100.204	209.16	1.620	−131.05	1.38989	396.8	512.7	0.0691	14
15	2–Methylhexane	C_7H_{16}	100.204	194.09	2.272	−180.89	1.38714	396.5	495.00	0.0673	15
16	3–Methylhexane	C_7H_{16}	100.204	197.33	2.131	———	1.39091	408.1	503.80	0.0646	16
17	3–Ethylpentane	C_7H_{16}	100.204	200.25	2.013	−181.48	1.39566	419.3	513.39	0.0665	17
18	2,2–Dimethylpentane	C_7H_{16}	100.204	174.54	3.494	−190.86	1.38446	402.2	477.23	0.0665	18
19	2,4–Dimethylpentane	C_7H_{16}	100.204	176.89	3.293	−182.63	1.38379	396.9	475.95	0.0668	19
20	3,3–Dimethylpentane	C_7H_{16}	100.204	186.91	2.774	−210.01	1.38564	427.2	505.87	0.0662	20
21	Triptane	C_7H_{16}	100.204	177.58	3.375	−12.81	1.39168	428.4	496.44	0.0636	21
22	n–Octane	C_8H_{18}	114.231	258.21	0.53694	−70.18	1.39956	360.7	564.22	0.0690	22
23	Diisobutyl	C_8H_{18}	114.231	228.39	1.102	−132.11	1.39461	360.6	530.44	0.0676	23
24	Isooctane	C_8H_{18}	114.231	210.63	1.709	−161.27	1.38624	372.4	519.46	0.0656	24
25	n–Nonane	C_9H_{20}	128.258	303.47	0.17953	−64.28	1.40746	331.8	610.68	0.0684	25
26	n–Decane	$C_{10}H_{22}$	142.285	345.48	0.06088	−21.36	1.41385	305.2	652.0	0.0679	26
27	Cyclopentane	C_5H_{10}	70.134	120.65	9.915	−136.91	1.40896	653.8	461.2	0.0594	27
28	Methylcyclopentane	C_6H_{12}	84.161	161.25	4.503	−224.40	1.41210	548.9	499.35	0.0607	28
29	Cyclohexane	C_6H_{12}	84.161	177.29	3.266	43.77	1.42862	590.8	536.6	0.0586	29
30	Methylcyclohexane	C_7H_{14}	98.188	213.68	1.609	−195.87	1.42538	503.5	570.27	0.0600	30

31	Ethene(Ethylene)	C_2H_4	28.054	−154.73	(1400)*	−272.47*	(1.228)*	731.0	48.54	0.0746	31
32	Propene(Propylene)	C_3H_6	42.081	−53.84	227.7	−301.45*	1.3130*	668.6	197.17	0.0689	32
33	1–Butene(Butylene)	C_4H_8	56.108	20.79	62.10	−301.63*	1.3494*	583.5	295.48	0.0685	33
34	cis–2–Butene	C_4H_8	56.108	38.69	45.95	−218.06	1.3665*	612.1	324.37	0.0668	34
35	trans–2–Butene	C_4H_8	56.108	33.58	49.87	−157.96	1.3563*	587.4	311.86	0.0679	35
36	Isobutene	C_4H_8	56.108	19.59	63.02	−220.65	1.3512*	580.2	292.55	0.0682	36
37	1–Pentene	C_5H_{10}	70.134	85.93	19.12	−265.39	1.37426	511.8	376.93	0.0676	37
38	1,2–Butadiene	C_4H_6	54.092	51.53	36.53	−213.16	—	(653.)*	(340.)*	(0.065)*	38
39	1,3–Butadiene	C_4H_6	54.092	24.06	59.46	−164.02	1.3975*	627.5	305.	0.0654	39
40	Isoprene	C_5H_8	68.119	93.31	16.68	−230.73	1.42498	(558.)*	(412.)*	(0.065)*	40
41	Acetylene	C_2H_2	26.038	−120.49*	—	−114.5*	—	890.4	95.34	0.0695	41
42	Benzene	C_6H_6	78.114	176.18	3.225	41.95	1.50396	710.4	552.22	0.0531	42
43	Toluene	C_7H_8	92.141	231.13	1.033	−139.00	1.49942	595.5	605.57	0.0550	43
44	Ethylbenzene	C_8H_{10}	106.167	277.16	0.3716	−138.966	1.49826	523.0	651.29	0.0565	44
45	o–Xylene	C_8H_{10}	106.167	291.97	0.2643	−13.59	1.50767	541.6	674.92	0.0557	45
46	m–Xylene	C_8H_{10}	106.167	282.41	0.3265	−54.18	1.49951	512.9	651.02	0.0567	46
47	p–Xylene	C_8H_{10}	106.167	281.07	0.3424	55.83	1.49810	509.2	649.54	0.0570	47
48	Styrene	C_8H_8	104.152	293.25	0.2582	−23.10	1.54937	587.8	(703.)*	0.0534	48
49	Isopropylbenzene	C_9H_{12}	120.194	306.34	0.1884	−140.814	1.49372	465.4	676.3	0.0572	49
50	Methyl alcohol	CH_4O	32.042	148.44	4.629	−143.79	1.33034	1174.	463.08	0.0590	50
51	Ethyl alcohol	C_2H_6O	46.069	172.90	2.312	−173.4	1.36346	890.1	465.39	0.0581	51
52	Carbon monoxide	CO	28.010	−312.68	—	−337.00*	1.00036*	507.5	−220.43	0.0532	52
53	Carbon dioxide	CO_2	44.010	−109.257*	—	−69.83*	1.00048*	1071.	87.91	0.0344	53
54	Hydrogen sulfide	H_2S	34.08	−76.497	394.59	−121.88*	1.00060*	1300.	212.45	0.0461	54
55	Sulfur dioxide	SO_2	64.06	14.11	85.46	−103.86*	1.00062*	1143.	315.8	0.0305	55
56	Ammonia	NH_3	17.0305	−27.99	211.9	−107.88*	1.00036*	1646.	270.2	0.0681	56
57	Air	N_2+O_2	28.9625	−317.8	—	—	1.00028*	546.9	−221.31	0.0517	57
58	Hydrogen	H_2	2.0159	−422.955*	—	−435.26*	1.00013*	188.1	−399.9	0.5165	58
59	Oxygen	O_2	31.9988	−297.332*	—	−361.820*	1.00027*	731.4	−181.43	0.0367	59
60	Nitrogen	N_2	28.0134	−320.451	—	−346.00*	1.00028*	493.1	−232.51	0.0510	60
61	Chlorine	Cl_2	70.906	−29.13	157.3	−149.73*	1.3878*	1157.	290.75	0.0280	61
62	Water	H_2O	18.0153	212.000*	0.9501	32.00	1.33335	3198.8	705.16	0.0497$_5$	62
63	Helium	He	4.0026	−452.09	—	—	1.00003*	32.99	−450.31	0.2300	63
64	Hydrogen chloride	HCl	36.461	−121.27	906.71	−173.52*	1.00042*	1205.	124.77	0.0356	64

TABLE 1–1 *continued*

Physical Constants

Number	See Note No. ->	K.					L.	M.	Flammability limits, vol % in air mixture		ASTM octane number		Number
	Compound	Heating value, 60°F					Heat of vaporization 14.696 psia at boiling point, Btu/lbm	Air required for combustion ideal gas $ft^3(air)/ft^3(gas)$	Lower	Higher	Motor method D-357	Research method D-908	
		Net		Gross									
		Btu/ft^3 Ideal gas, 14.696 psia	Btu/lbm Liquid	Btu/ft^3 ideal gas, 14.696 psia	Btu/lbm Liquid	Btu/gal. Liquid							
1	Methane	909.4	——	1010.0	——	——	219.45	9.548	5.0	15.0	——	——	1
2	Ethane	1618.7	20277.*	1769.6	22181.*	65869.*	211.14	16.710	2.9	13.0	+0.05	+1.6*	2
3	Propane	2314.9	19757.*	2516.1	21489.*	90830.*	183.01	23.871	2.0	9.5	97.1	+1.8*	3
4	Isobutane	3000.4	19437.*	3251.9	21079.*	98917.*	157.23	31.032	1.8	8.5	97.6	+0.1*	4
5	n-Butane	3010.8	19494.*	3262.3	21136.*	102911.*	165.93	31.032	1.5	9.0	89.6*	93.8*	5
6	Isopentane	3699.0	19303.	4000.9	20891.	108805.	147.12	38.193	1.3	8.0	90.3	92.3	6
7	n-Pentane	3706.9	19335.	4008.9	20923.	110091.	153.57	38.193	1.4	8.3	62.6*	61.7*	7
8	Neopentane	3682.9	19235.*	3984.7	20822.*	103577.*	135.58	38.193	1.3	7.5	80.2	85.5	8
9	n-Hexane	4403.8	19232.	4755.9	20783.	115021.	143.94	45.355	1.1	7.7	26.0	24.8	9
10	2-Methylpentane	4395.2	19202.	4747.3	20753.	113822.	138.45	45.355	1.18	7.0	73.5	73.4	10
11	3-Methylpentane	4398.2	19213.	4750.3	20764.	115813.	140.05	45.355	1.2	7.7	74.3	74.5	11
12	Neohexane	4384.0	19163.	4736.2	20714.	112916.	131.23	45.355	1.2	7.0	93.4	91.8	12
13	2,3-Dimethylbutane	4392.9	19195.	4745.0	20746.	115246.	136.07	45.355	1.2	7.0	94.3	+0.3	13
14	n-Heptane	5100.0	19155.	5502.5	20679.	118648.	136.00	52.516	1.0	7.0	0.0	0.0	14
15	2-Methylhexane	5092.2	19133.	5494.6	20657.	117644.	131.58	52.516	1.0	7.0	46.4	42.4	15
16	3-Methylhexane	5096.0	19146.	5498.6	20671.	119197.	132.10	52.516	(1.01)	(6.6)	55.8	52.0	16
17	3-Ethylpentane	5098.3	19154.	5500.7	20679.	121158.	132.82	52.516	(1.00)	(6.5)	69.3	65.0	17
18	2,2-Dimethylpentane	5079.6	19095.	5481.9	20620.	116606.	125.12	52.516	(1.09)	(6.8)	95.6	92.8	18
19	2,4-Dimethylpentane	5084.2	19111.	5486.7	20635.	116526.	126.57	52.516	(1.08)	(6.8)	83.8	83.1	19
20	3,3-Dimethylpentane	5086.4	19119.	5488.8	20643.	120080.	127.20	52.516	(1.04)	(7.0)	86.6	80.8	20
21	Triptane	5081.2	19103.	5483.5	20628.	119451.	124.21	52.516	(1.08)	(6.8)	+0.1	+1.8	21
22	n-Octane	5796.1	19096.	6248.9	20601.	121422.	129.52	59.677	0.8	6.5	——	——	22
23	Diisobutyl	5780.5	19047.	6233.5	20552.	119586.	122.83	59.677	(0.92)	(6.3)	55.7	55.2	23
24	Isooctane	5778.8	19063.	6231.7	20568.	119389.	112.94	59.677	0.95	6.0	100.0	100.0	24
25	n-Nonane	6493.2	19054.	6996.5	20543.	123634.	124.36	66.839	0.7	5.6	——	——	25
26	n-Decane	7189.6	19018.	7742.9	20494.	125448.	119.65	74.000	0.7	5.4	——	——	26
27	Cyclopentane	3512.1	18825.	3763.7	20186.	126304.	167.33	35.806	(1.48)	(8.3)	84.9*	+0.1	27
28	Methylcyclopentane	4199.4	18771.	4501.2	20132.	126467.	148.54	42.968	1.0	8.35	80.0	91.3	28
29	Cyclohexane	4179.7	18675.	4481.7	20036.	130873.	153.03	42.968	1.2	8.35	77.2	83.0	29
30	Methylcyclohexane	4863.6	18640.	5215.9	20002.	129071.	136.30	50.129	1.1	6.7	71.1	74.8	30

31	Ethene(Ethylene)	1499.1	——	1599.8	——	——	207.41	14.323	2.7	36.0	75.6	+0.03	31
32	Propene(Propylene)	2181.8	(19858.)	2332.7	(21208.)	(92113.)	188.19	21.484	2.0	11.7	84.9	+0.2	32
33	1-Butene(Butylene)	2878.7	19309.*	3079.9	20670.*	103582.*	167.96	28.645	1.6	10.	80.8*	97.4	33
34	cis-2-Butene	2871.0	19241.*	3072.2	20602.*	107724.*	178.89	28.645	1.6	10.	83.5	100.0	34
35	trans-2-Butene	2866.8	19221.*	3068.0	20582.*	104666.*	174.37	28.645	1.6	10.	——	——	35
36	Isobutene	2859.9	19182.*	3061.1	20543.*	102830.*	169.47	28.645	1.6	10.	——	——	36
37	1-Pentene	3575.0	19184.	3826.5	20545.	110602.	154.48	35.806	1.3	10.	77.1	90.9	37
38	1,2-Butadiene	2789.0	19378.*	2939.9	20437.*	112111.*	191.88	26.258	(1.62)	(10.3)	——	——	38
39	1,3-Butadiene	2729.0	18967.*	2879.9	20025.*	104717.*	185.29	26.258	2.0	12.5	——	——	39
40	Isoprene	3410.8	18832.	3612.1	19953.	114141.	163.48	33.419	(1.12)	(8.5)	81.0	99.1	40
41	Acetylene	1423.2	(20887.)	1473.5	(21613.)	(75204.)	151.90	11.935	1.5	100.	——	——	41
42	Benzene	3590.9	17256.	3741.8	17989.	132651.	169.24	35.806	1.2	8.0	+2.8	——	42
43	Toluene	4273.6	17421.	4475.0	18250.	132661.	154.83	42.968	1.2	7.1	+0.3	+5.8	43
44	Ethylbenzene	4970.5	17593.	5222.2	18492.	134387.	144.02	50.129	1.0	8.0	97.9	+0.8	44
45	o-Xylene	4958.2	17544.	5209.9	18444.	136036.	149.10	50.129	1.0	7.6	100.0	——	45
46	m-Xylene	4956.3	17541.	5207.9	18440.	133559.	147.24	50.129	1.0	7.0	+2.8	+4.0	46
47	p-Xylene	4957.1	17545.	5208.8	18444.	133131.	145.71	50.129	1.0	7.0	+1.2	+3.4	47
48	Styrene	4829.8	17414.	5031.1	18147.	137841.	152.85	47.742	1.1	8.0	+0.2	>+3.*	48
49	Isopropylbenzene	5660.9	17709.	5962.8	18662.	134792.	134.24	57.290	0.8	6.5	99.3	+2.1	49
50	Methyl alcohol	766.1	8559.	866.7	9751.	64731.	462.58	7.161	5.5	44.0	——	——	50
51	Ethyl alcohol	1448.1	11530.	1599.1	12770.	84539.	359.07	14.323	3.28	19.0	——	——	51
52	Carbon monoxide	320.5	——	320.5	——	——	92.77	2.387	12.50	74.20	——	——	52
53	Carbon dioxide	0.0	——	0.0	——	——	246.47*	——	——	——	——	——	53
54	Hydrogen sulfide	586.8	6337.*	637.1	6897.*	46086.*	235.63	7.161	4.30	45.50	——	——	54
55	Sulfur dioxide	0.0	——	0.0	——	——	167.22	——	——	——	——	——	55
56	Ammonia	359.0	——	434.4	——	——	589.48	3.581	15.50	27.00	——	——	56
57	Air	0.0	——	0.0	——	——	88.20	——	——	——	——	——	57
58	Hydrogen	273.8	——	324.2	——	——	192.74	2.387	4.00	74.20	——	——	58
59	Oxygen	0.0	——	0.0	——	——	91.59	——	——	——	——	——	59
60	Nitrogen	0.0	——	0.0	——	——	85.59	——	——	——	——	——	60
61	Chlorine	——	——	——	——	——	123.75	——	——	——	——	——	61
62	Water	0.0	*	*	0.0	0.0	970.18	——	——	——	——	——	62
63	Helium	0.0	——	0.0	——	——	——	——	——	——	——	——	63
64	Hydrogen chloride	——	——	——	——	——	190.43	——	——	——	——	——	64

Note: Numbers in this table do not have accuracies greater than1 part in 1000; in some cases extra digits have been added to calculated values to achieve consistency or to permit recalculation of experimental values.

Source: GSPA Engineers Data Book, 10th ed. Tulsa, OK: Gas Processors Suppliers Association, 1987. Courtesy of the Gas Processors Suppliers Association.

A method that is particularly convenient for plotting the vapor pressure as a function of temperature for pure substances is shown in Figure 1–3. The chart is known as a Cox chart. Note that the vapor pressure scale is logarithmic, while the temperature scale is entirely arbitrary.

EXAMPLE 1–1

A pure propane is held in a laboratory cell at 80°F and 200 psia. Determine the "existence state" (i.e., as a gas or liquid) of the substance.

SOLUTION

From a Cox chart, the vapor pressure of propane is read as $p_v = 150$ psi, and because the laboratory cell pressure is 200 psi (i.e., $p > p_v$), this means that the laboratory cell contains a liquefied propane.

The vapor pressure chart as presented in Figure 1–3 allows a quick estimation of the vapor pressure p_v of a pure substance at a specific temperature. For computer applications, however, an equation is more convenient. Lee and Kesler (1975) proposed the following generalized vapor pressure equation:

$$p_v = p_c \exp(A + \omega B) \tag{1–3}$$

with

$$A = 5.92714 - \frac{6.09648}{T_r} - 1.2886 \ln(T_r) + 0.16934(T_r)^6 \tag{1–4}$$

$$B = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.4357(T_r)^6 \tag{1–5}$$

The term T_r, called the *reduced temperature*, is defined as the ratio of the absolute system temperature to the critical temperature of the fraction, or

$$T_\mathrm{r} = \frac{T}{T_c}$$

where

T_r = reduced temperature
T = substance temperature, °R
T_c = critical temperature of the substance, °R
p_c = critical pressure of the substance, psia
ω = acentric factor of the substance

The acentric factor ω was introduced by Pitzer (1955) as a correlating parameter to characterize the centricity or nonsphericity of a molecule, defined by the following expression:

$$\omega = -\log\left(\frac{p_v}{p_c}\right)_{T=0.7T_c} - 1 \tag{1–6}$$

where

p_c = critical pressure of the substance, psia

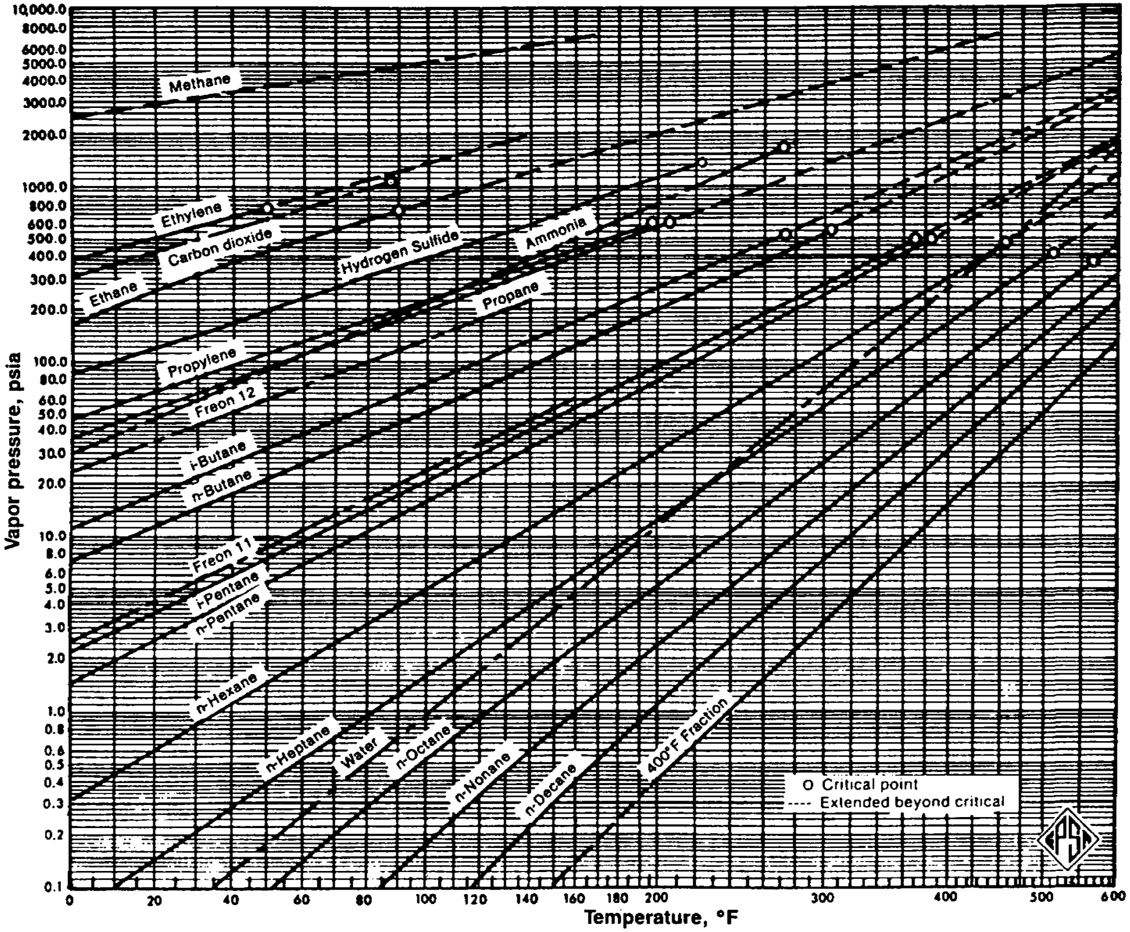


FIGURE 1–3 *Vapor pressure chart for hydrocarbon components.*

Source: GPSA Engineering Data Book, 10th ed. Tulsa, OK: Gas Processors Suppliers Association, 1987. Courtesy of the Gas Processors Suppliers Association.

p_v = vapor pressure of the substance at a temperature equal to 70% of the substance critical temperature (i.e., $T = 0.7T_c$), psia

The acentric factor frequently is used as a third parameter in corresponding states and equation-of-state correlations. Values of the acentric factor for pure substances are tabulated in Table 1–1.

EXAMPLE 1–2

Calculate the vapor pressure of propane at 80°F by using the Lee and Kesler correlation.

SOLUTION

Obtain the critical properties and the acentric factor of propane from Table 1–1:

$T_c = 666.01°\text{R}$
$p_c = 616.3$ psia
$\omega = 0.1522$

Calculate the reduced temperature:

$$T_r = \frac{T}{T_c} = \frac{540}{666.01} = 0.81108$$

Solve for the parameters A and B by applying equations (1–4) and (1–5), respectively, to give

$$A = 5.92714 - \frac{6.09648}{T_r} - 1.2886 \ln(T_r) + 0.16934(T_r)^6$$

$$A = 5.92714 - \frac{6.09648}{0.81108} - 1.2886 \ln(0.81108) + .16934(0.81108)^6 = -1.273590$$

$$B = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.4357(T_r)^6$$

$$B = 15.2518 - \frac{15.6875}{0.81108} - 13.4721 \ln(0.81108) + 0.4357(0.81108)^6 = -1.147045$$

Solve for p_v by applying equation (1–3):

$$p_v = p_c \exp(A + \omega B)$$

$$p_v = (616.3) \exp[-1.27359 + 0.1572(-1.147045)] = 145 \text{ psia}$$

The densities of the saturated phases of a pure component (i.e., densities of the coexisting liquid and vapor) may be plotted as a function of temperature, as shown in Figure 1–4. Note that, for increasing temperature, the density of the saturated liquid is decreasing, while the density of the saturated vapor increases. At the critical point C, the densities of vapor and liquid converge at the *critical density* of the pure substance, that is, ρ_c. At this critical point C, all other properties of the phases become identical, such as viscosity, weight, and density.

Figure 1–4 illustrates a useful observation, the law of the rectilinear diameter, which states that the arithmetic average of the densities of the liquid and vapor phases is a linear function of the temperature. The straight line of average density versus temperature makes an easily defined intersection with the curved line of densities. This intersection

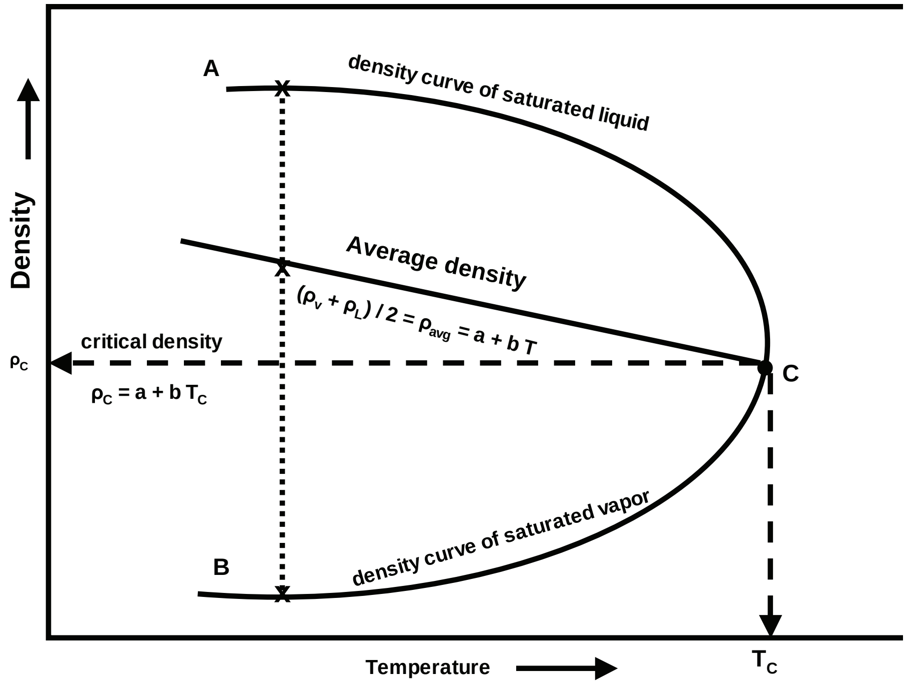


FIGURE 1–4 *Typical temperature/density diagram.*

then gives the critical temperature and density. Mathematically, this relationship is expressed as follows:

$$\frac{\rho_v + \rho_L}{2} = \rho_{avg} = a + bT \tag{1–7}$$

where

ρ_v = density of the saturated vapor, lb/ft^3
ρ_L = density of the saturated liquid, lb/ft^3
ρ_{avg} = arithmetic average density, lb/ft^3
T = temperature, °R
a, b = intercept and slope of the straight line

Since, at the critical point, ρ_v and ρ_L are identical, equation (1–7) can be expressed in terms of the critical density as follows:

$$\rho_c = a + bT_c \tag{1–8}$$

where ρ_c = critical density of the substance, lb/ft^3. Combining equation (1–7) with (1–8) and solving for the critical density gives

$$\rho_c = \left[\frac{a + bT}{a + bT_c}\right]\rho_{avg}$$

This density-temperature diagram is useful in calculating the critical volume from density data. The experimental determination of the critical volume sometimes is difficult, since it requires the precise measurement of a volume at a high temperature and pressure.

However, it is apparent that the straight line obtained by plotting the average density versus temperature intersects the critical temperature at the critical density. The molal critical volume is obtained by dividing the molecular weight by the critical density:

$$V_c = \frac{M}{\rho_c}$$

where

V_c = critical volume of pure component, $\text{ft}^3/\text{lb}_m - \text{mol}$
M = molecular weight, $\text{lb}_m/\text{lb}_m - \text{mol}$
ρ_c = critical density, lb_m/ft^3

Figure 1–5 shows the saturated densities for a number of fluids of interest to the petroleum engineer. Note that, for each pure substance, the upper curve is termed the *saturated liquid density curve*, while the lower curve is labeled the *saturated vapor density curve*. Both curves meet and terminate at the critical point represented by a "dot" in the diagram.

EXAMPLE 1–3

Calculate the saturated liquid and gas densities of n-butane at 200°F.

SOLUTION

From Figure 1–5, read both values of liquid and vapor densities at 200°F to give

Liquid density $\rho_L = 0.475 \text{ gm/cm}^3$
Vapor density $\rho_v = 0.035 \text{ gm/cm}^3$

The density-temperature diagram also can be used to determine the state of a single-component system. Suppose the *overall* density of the system, ρ_t, is known at a given temperature. If this overall density is less than or equal to $\rho_{v,}$ it is obvious that the system is composed entirely of vapor. Similarly, if the overall density ρ_t is greater than or equal to ρ_L, the system is composed entirely of liquid. If, however, the overall density is between ρ_L and ρ_v, it is apparent that both liquid and vapor are present. To calculate the weights of liquid and vapor present, the following volume and weight balances are imposed:

$$m_L + m_v = m_t$$
$$V_L + V_v = V_t$$

where

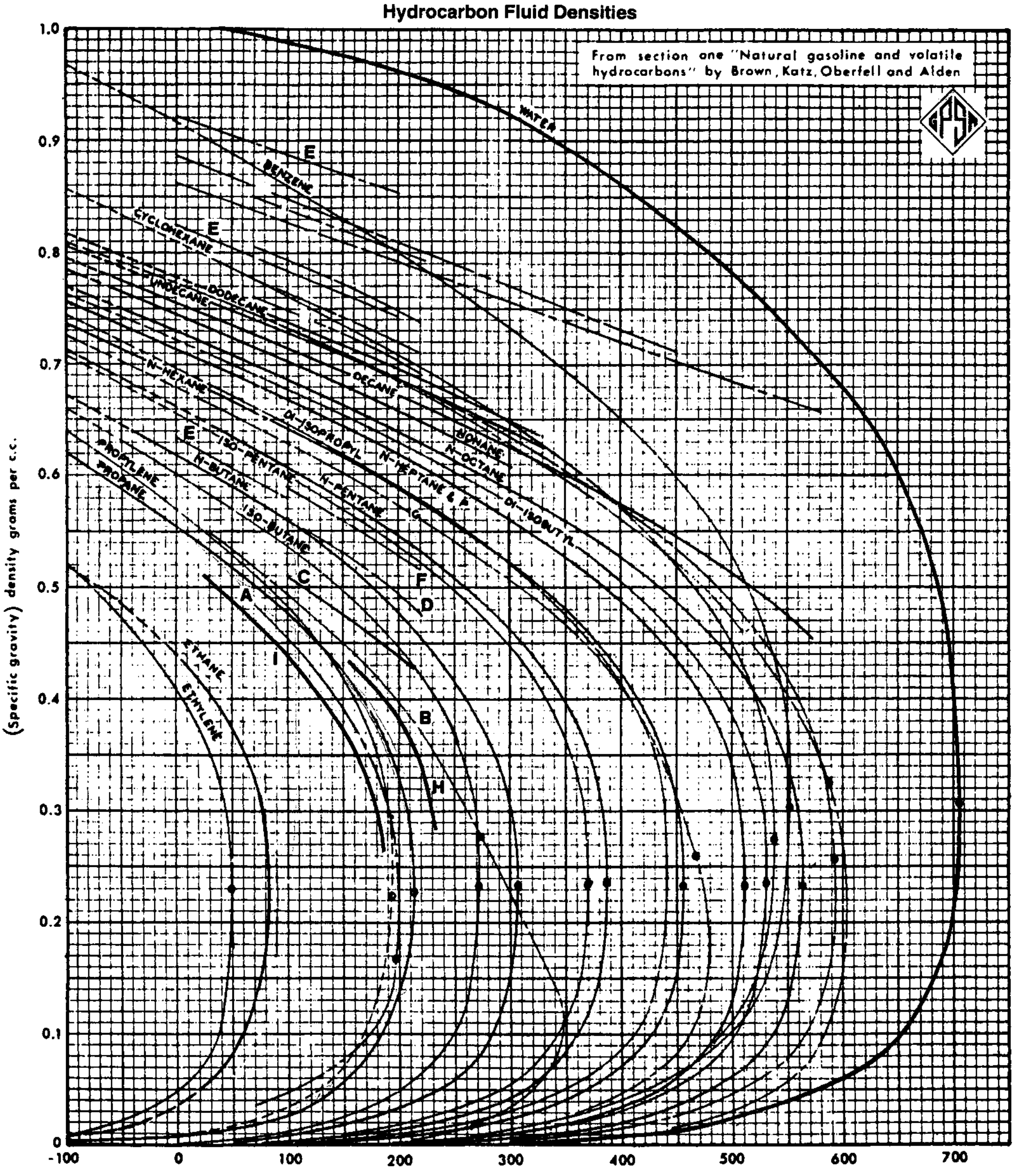
m_L, m_v, and m_t = the mass of the liquid, vapor, and total system, respectively
V_L, V_v, and V_t = the volume of the liquid, vapor, and total system, respectively

Combining the two equations and introducing the density into the resulting equation gives

$$\frac{m_t - m_v}{\rho_L} + \frac{m_v}{\rho_v} = V_t \tag{1–9}$$

EXAMPLE 1–4

Ten pounds of a hydrocarbon are placed in a 1 ft³ vessel at 60°F. The densities of the coexisting liquid and vapor are known to be 25 lb/ft³ and 0.05/ft³, respectively, at this temperature. Calculate the weights and volumes of the liquid and vapor phases.



Identification

- A 8 mol % CH_4—92 mol % C_3H_8 (370-739 lbs.)
- B 50.25 wt. % C_2H_6—49.75 wt. % n-C_7H_{16}
- C 19.2 wt. % CH_4—80.8 wt. % C_6H_{14} (2412-2506 lbs.)
- D 7.15 wt. % CH_4—92.85 wt. % n-C_5H_{12} (854-1043 lbs.)
- E National Standard Petroleum Oil Tables
- F 7.15 wt. % CH_4—92.85 wt. % n % C_5H_{12} (at 3000 lbs.)
- G 9.78 wt. % C_2H_6—90.22 wt. % n-C_7H_{16}
- H 75.45 mole % C_3H_8—24.55 % nC_4H_{10} (ref 4)
- I 65.77 mole % C_2H_6—34.23 % nC_4H_{10} (ref 3)

FIGURE 1–5 *Hydrocarbon fluid densities.*

Source: GPSA Engineering Data Book, 10th ed. Tulsa, OK: Gas Processors Suppliers Association, 1987. Courtesy of the Gas Processors Suppliers Association.

SOLUTION

Step 1 Calculate the density of the overall system:

$$\rho_t = \frac{m_t}{V_t} = \frac{10}{1.0} = 10 \text{ lb/ft}^3$$

Step 2 Since the overall density of the system is between the density of the liquid and the density of the gas, the system must be made up of both liquid and vapor.

Step 3 Calculate the weight of the vapor from equation (1–9):

$$\frac{10 - m_v}{25} + \frac{m_v}{0.05} = 1$$

Solving the above equation for m_v, gives

$$m_v = 0.030 \text{ lb}$$
$$m_L = 10 - m_v = 10 - 0.03 = 9.97 \text{ lb}$$

Step 4 Calculate the volume of the vapor and liquid phases:

$$V_v = \frac{m_v}{\rho_v} = \frac{0.03}{0.05} = 0.6 \text{ ft}^3$$
$$V_L = V_t - V_v = 1 - 0.6 = 0.4 \text{ ft}^3$$

EXAMPLE 1–5

A utility company stored 58 million lbs, that is $m_t = 58{,}000{,}000$ lb, of propane in a washed-out underground salt cavern of volume 480,000 bbl ($V_t = 480{,}000$ bbl) at a temperature of 110°F. Estimate the weight and volume of liquid propane in storage in the cavern.

SOLUTION

Step 1 Calculate the volume of the cavern in ft^3:

$$V_t = (480{,}000)(5.615) = 2{,}695{,}200 \text{ ft}^3$$

Step 2 Calculate the total density of the system:

$$\rho_t = \frac{m_t}{V_t} = \frac{58{,}000{,}000}{2{,}695{,}200} = 21.52 \text{ lb/ft}^3$$

Step 3 Determine the saturated densities of propane from the density chart of Figure 1–5 at 110°F:

$$\rho_L = 0.468 \text{ gm/cm}^3 = (0.468)(62.4) = 29.20 \text{ lb/ft}^3$$
$$\rho_v = 0.03 \text{ gm/cm}^3 = (0.03)(62.4) = 1.87 \text{ lb/ft}^3$$

Step 4 Test for the existing phases. Since

$$\rho_v < \rho_t < \rho_L$$
$$1.87 < 21.52 < 29.20$$

both liquid and vapor are present.

Step 5 Solve for the weight of the vapor phase by applying equation (1–9)

$$\frac{58{,}000{,}000 - m_v}{29.20} + \frac{m_v}{1.87} = 2{,}695{,}200$$

$m_v = 1{,}416{,}345$ lb

$$V_v = \frac{m_v}{\rho} = \frac{1{,}416{,}345}{1.87} = 757{,}404 \text{ ft}^3$$

Step 6 Solve for the volume and weight of propane:

$V_L = V_t - V_v = 2{,}695{,}200 - 757{,}404 = 1{,}937{,}796$ ft^3 (72% of total volume);
$m_L = m_t - m_v = 58{,}000{,}000 - 1{,}416{,}345 = 56{,}583{,}655$ lb (98% of total weight).

The example demonstrates the simplest case of phase separation, that of a pure component. In general, petroleum engineers are concerned with calculating phase separations of complex mixtures representing crude oil, natural gas, and condensates.

Rackett (1970) proposed a simple generalized equation for predicting the saturated liquid density, ρ_L, of pure compounds. Rackett expressed the relation in the following form:

$$\rho_L = \frac{Mp_c}{RT_c Z_c^a} \tag{1–10}$$

with the exponent *a* given as

$a = 1 + (1 - T_r)^{2/7}$

where

M = molecular weight of the pure substance
p_c = critical pressure of the substance, psia
T_c = critical temperature of the substance, °R
Z_c = critical gas compressibility factor;
R = gas constant , 10.73 ft^3 psia/lb-mole, °R
$T_r = \dfrac{T}{T_c}$, reduced temperature
T = temperature, °R

Spencer and Danner (1973) modified Rackett's correlation by replacing the critical compressibility factor Z_c in equation (1–9) with a parameter called *Rackett's compressibility factor*, Z_{RA}, that is a unique constant for each compound. The authors proposed the following modification of the Rackett equation:

$$\rho_L = \frac{Mp_c}{RT_c (Z_{RA})^a} \tag{1–11}$$

with the exponent *a* as defined previously by

$a = 1 + (1 + T_r)^{2/7}$

The values of Z_{RA} are given in Table 1–2 for selected components.

If a value of Z_{RA} is not available, it can be estimated from a correlation proposed by Yamada and Gunn (1973) as

$$Z_{RA} = 0.29056 - 0.08775\omega \tag{1–12}$$

where ω is the acentric factor of the compound.

TABLE 1–2 *Values of* Z_{RA} *for Selected Pure Components*

Carbon dioxide	0.2722	n-pentane	0.2684
Nitrogen	0.2900	n-hexane	0.2635
Hydrogen sulfide	0.2855	n-heptanes	0.2604
Methane	0.2892	i-octane	0.2684
Ethane	0.2808	n-octane	0.2571
Propane	0.2766	n-nonane	0.2543
i-butane	0.2754	n-decane	0.2507
n-butane	0.2730	n-undecane	0.2499
i-Pentane	0.2717		

EXAMPLE 1–6

Calculate the saturated liquid density of propane at 160°F by using (1) the Rackett correlation and (2) the modified Rackett equation.

SOLUTION

Find the critical properties of propane from Table 1–1, to give

$T_c = 666.06°\text{R}$
$p_c = 616.0$ psia
$M = 44.097$
$V_c = 0.0727\ \text{ft}^3/\text{lb}$

Calculate Z_c by applying the real gas equation of state:

$$Z = \frac{pv}{nRT} = \frac{pv}{(m/M)RT}$$

or

$$Z = \frac{pVM}{RT}$$

where v = substance volume, ft^3, and V = substance volume, ft^3/lb, at the critical point:

$$Z_c = \frac{p_c V_c M}{RT_c}$$

$$Z_c = \frac{(616.0)(0.0727)(44.097)}{(10.73)(666.06)} = 0.2763$$

$$T_r = \frac{T}{T_c} = \frac{160 + 460}{666.06} = 0.93085$$

For the Rackett correlation, solve for the saturated liquid density by applying the Rackett equation, equation (1–10):

$$a = 1 + (1 - T_r)^{2/7} = 1 + (1 - 0.93085)^{2/7} = 1.4661$$

$$\rho_L = \frac{Mp_c}{RT_c Z_c^a}$$

$$\rho_L = \frac{(44.097)(616.0)}{(10.73)(666.06)(0.2763)^{1.4661}}$$

For the modified Rackett equation, from Table 1–2, find the Rackett compressibility factor $Z_{RA} = 0.2766$; then, the modified Rackett equation, equation (1–11); gives

$$\rho_L = \frac{(44.097)(616.0)}{(10.73)(666.06)(0.2766)^{1.4661}} = 25.01 \text{ lb/ft}^3$$

Two-Component Systems

A distinguishing feature of the single-component system is that, at a fixed temperature, two phases (vapor and liquid) can exist in equilibrium at only one pressure; this is the vapor pressure. For a binary system, two phases can exist in equilibrium at various pressures at the same temperature. The following discussion concerning the description of the phase behavior of a two-component system involves many concepts that apply to the more complex multicomponent mixtures of oils and gases.

An important characteristic of binary systems is the variation of their thermodynamic and physical properties with the composition. Therefore, it is necessary to specify the composition of the mixture in terms of mole or weight fractions. It is customary to designate one of the components as the more volatile component and the other the less volatile component, depending on their relative vapor pressure at a given temperature.

Suppose that the examples previously described for a pure component are repeated, but this time we introduce into the cylinder a binary mixture of a known overall composition. Consider that the initial pressure p_1 exerted on the system, at a fixed temperature of T_1, is low enough that the entire system exists in the vapor state. This initial condition of pressure and temperature acting on the mixture is represented by point 1 on the p/V diagram of Figure 1–6. As the pressure is increased isothermally, it reaches point 2, at which an infinitesimal amount of liquid is condensed. The pressure at this point is called the *dew-point pressure*, p_d, of the mixture. It should be noted that, at the dew-point pressure, the composition of the vapor phase is equal to the overall composition of the binary mixture. As the total volume is decreased by forcing the piston inside the cylinder, a noticeable increase in the pressure is observed as more and more liquid is condensed. This condensation process is continued until the pressure reaches point 3, at which traces of gas remain. At point 3, the corresponding pressure is called the *bubble-point pressure*, p_b. Because, at the bubble point, the gas phase is only of infinitesimal volume, the composition of the liquid phase therefore is identical with that of the whole system. As the piston is forced further into the cylinder, the pressure rises steeply to point 4 with a corresponding decreasing volume.

Repeating the previous examples at progressively increasing temperatures, a complete set of isotherms is obtained on the p/V diagram of Figure 1–7 for a binary system consisting of n-pentane and n-heptane. The bubble-point curve, as represented by line *AC*, represents the locus of the points of pressure and volume at which the first bubble of gas is formed. The dew-point curve (line *BC*) describes the locus of the points of pressure and volume at which the first droplet of liquid is formed. The two curves meet at the critical

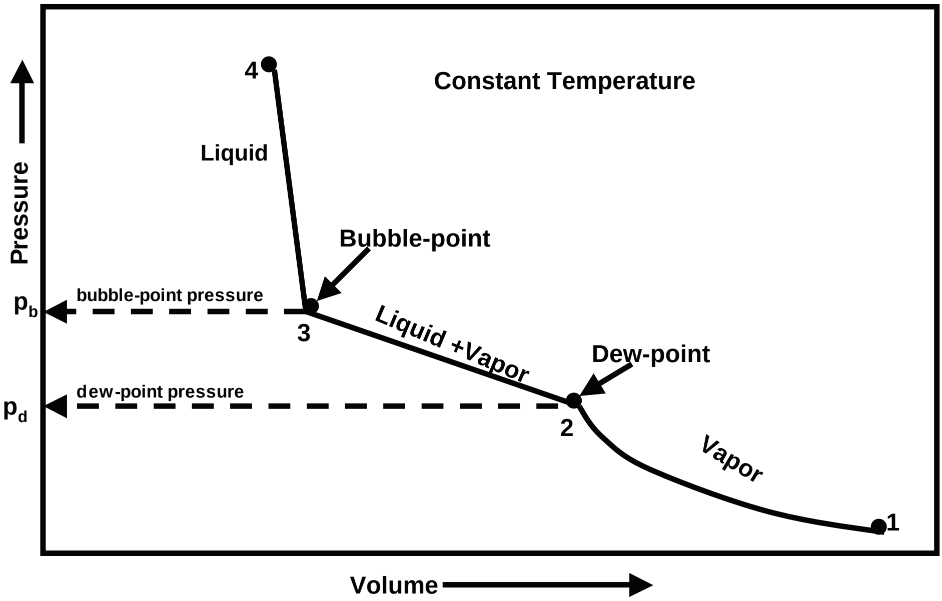


FIGURE 1–6 *Pressure/volume isotherm for a two-component system.*

point (point *C*). The critical pressure, temperature, and volume are given by p_c, T_c, and V_c, respectively. Any point within the phase envelope (line *ACB*) represents a system consisting of two phases. Outside the phase envelope, only one phase can exist.

If the bubble-point pressure and dew-point pressure for the various isotherms on a p/V diagram are plotted as a function of temperature, a p/T diagram similar to that shown in Figure 1–8 is obtained. Figure 1–8 indicates that the pressure/temperature relationships no longer can be represented by a simple vapor pressure curve, as in the case of a single-component system, but take on the form illustrated in the figure by the phase envelope *ACB*. The dashed lines within the phase envelope are called *quality lines*; they describe the pressure and temperature conditions of equal volumes of liquid. Obviously, the bubble-point curve and the dew-point curve represent 100% and 0% liquid, respectively.

Figure 1–9 demonstrates the effect of changing the composition of the binary system on the shape and location of the phase envelope. Two of the lines shown in the figure represent the vapor-pressure curves for methane and ethane, which terminate at the critical point. Ten phase boundary curves (phase envelopes) for various mixtures of methane and ethane also are shown. These curves pass continuously from the vapor-pressure curve of the one pure component to that of the other as the composition is varied. The points labeled 1–10 represent the critical points of the mixtures as defined in the legend of Figure 1–9. The dashed curve illustrates the locus of critical points for the binary system.

It should be noted by examining Figure 1–9 that, when one of the constituents becomes predominant, the binary mixture tends to exhibit a relatively narrow phase envelope and displays critical properties close to the predominant component. The size of the phase envelope enlarges noticeably as the composition of the mixture becomes evenly distributed between the two components.

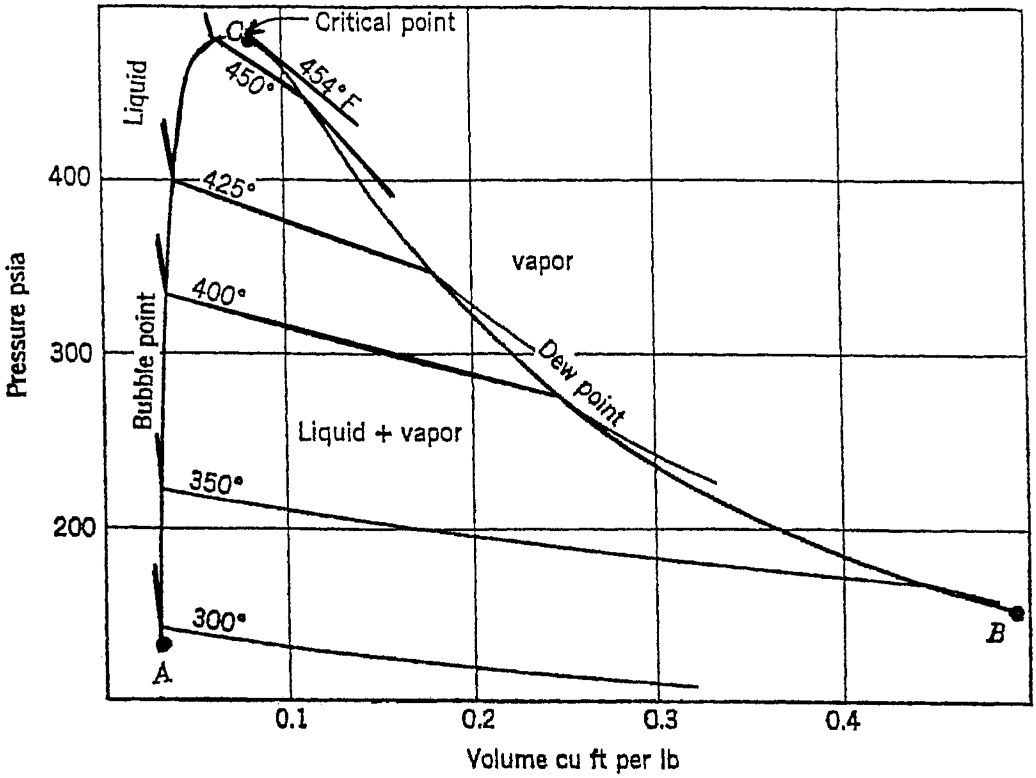


FIGURE 1–7 *Pressure/volume diagram for the n-pentane and n-heptane system containing 52.4 wt % n-heptane.*

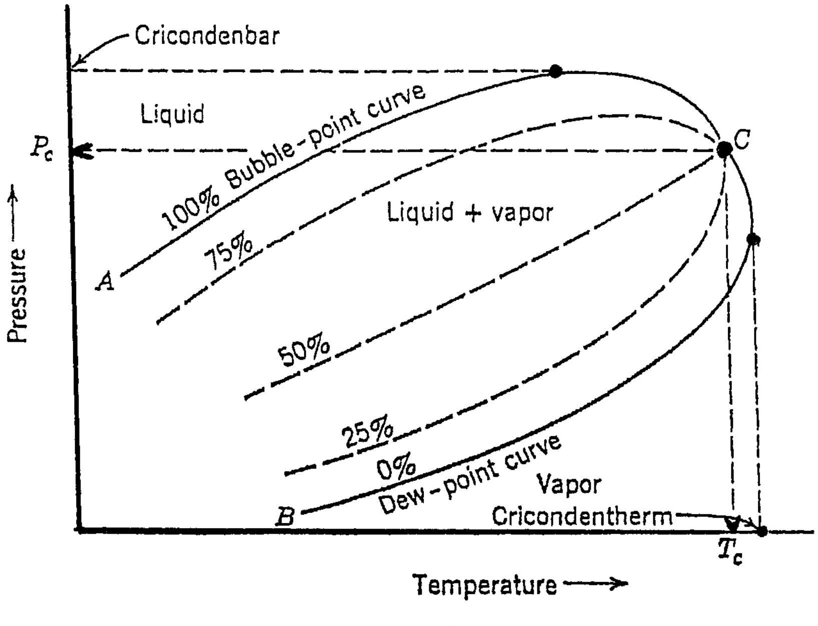


FIGURE 1–8 *Typical temperature/pressure diagram for a two-component system.*

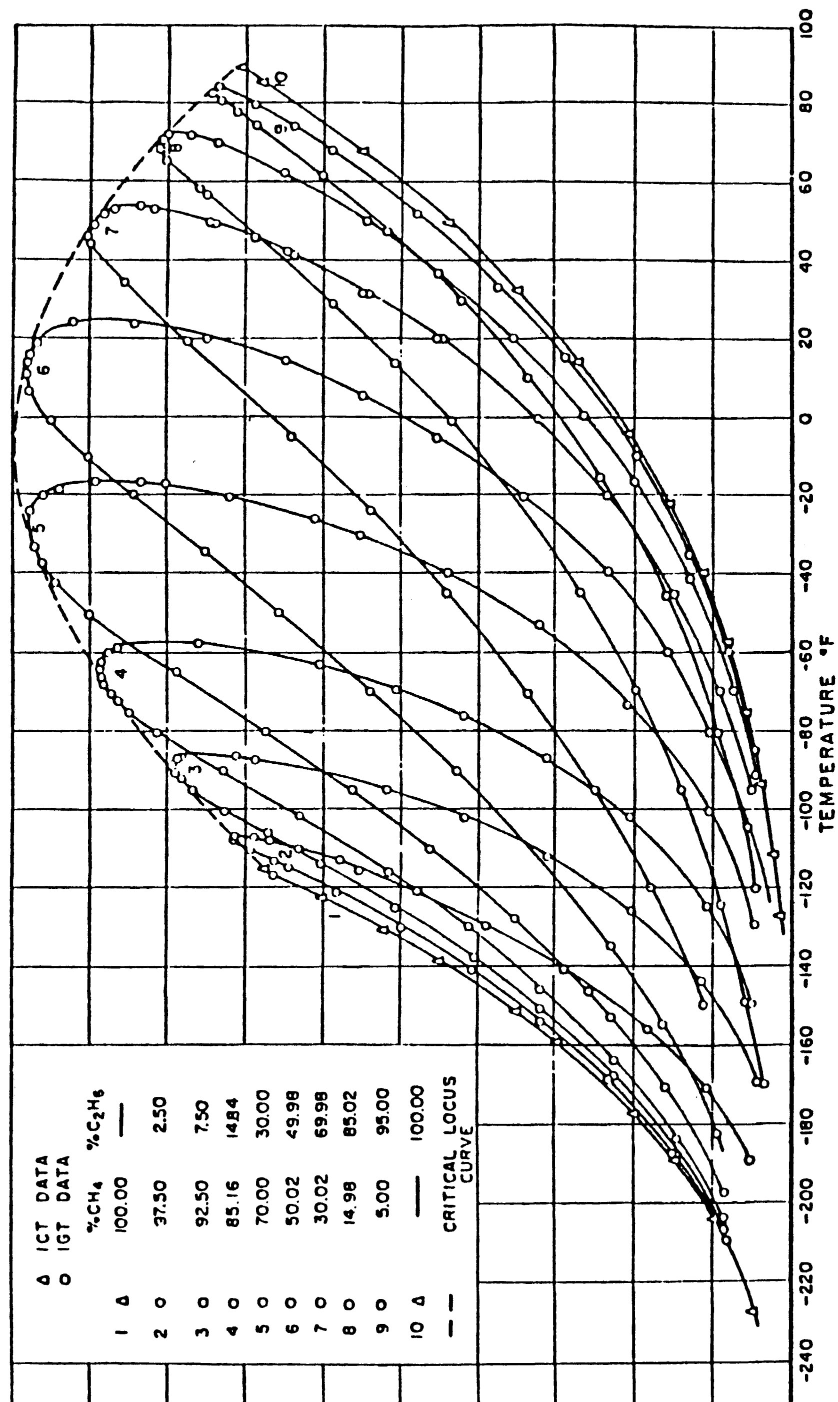


FIGURE 1–9 *Phase diagram of a methane/ethane mixture.*

Courtesy of the Institute of Gas Technology.

Figure 1–10 shows the critical loci for a number of common binary systems. Obviously, the critical pressure of mixtures is considerably higher than the critical pressure of the components in the mixtures. The greater the difference in the boiling point of the two substances, the higher the critical pressure of the mixture.

Pressure/Composition Diagram for Binary Systems

As pointed out by Burcik (1957), the pressure/composition diagram, commonly called the *p/x diagram*, is another means of describing the phase behavior of a binary system, as its overall composition changes at a constant temperature. It is constructed by plotting the dew-point and bubble-point pressures as a function of composition.

The bubble-point and dew-point lines of a binary system are drawn through the points that represent these pressures as the composition of the system is changed at a constant temperature. As illustrated by Burcik (1957), Figure 1–11 represents a typical pressure/composition diagram for a two-component system. Component 1 is described as the more volatile fraction and component 2 as the less volatile fraction. Point *A* in the figure represents the vapor pressure (dew point, bubble point) of the more volatile component, while point *B* represent that of the less volatile component. Assuming a composition of 75% by weight of component 1 (i.e., the more volatile component) and 25% of component 2, this mixture is characterized by a dew-point pressure represented as point *C* and a bubble-point pressure of point *D*. Different combinations of the two components produce different values for the bubble-point and dew-point pressures. The curve *ADYB* represents the bubble-point pressure curve for the binary system as a function of composition, while the line *ACXB* describes the changes in the dew-point pressure as the composition of the system changes at a constant temperature. The area below the dew-point line represents vapor, the area above the bubble-point line represents liquid, and the area between these two curves represents the two-phase region, where liquid and vapor coexist.

In the diagram in Figure 1–11, the composition is expressed in weight percent of the less volatile component. It is to be understood that the composition may be expressed equally well in terms of weight percent of the more volatile component, in which case the bubble-point and dew-point lines have the opposite slope. Furthermore, the composition may be expressed in terms of mole percent or mole fraction as well.

The points *X* and *Y* at the extremities of the horizontal line *XY* represent the composition of the coexisting of the vapor phase (point *X*) and the liquid phase (point *Y*) that exist in equilibrium at the same pressure. In other words, at the pressure represented by the horizontal line *XY*, the compositions of the vapor and liquid that coexist in the two-phase region are given by w_v and w_L, and they represent the weight percentages of the less volatile component in the vapor and liquid, respectively.

In the *p/x* diagram shown in Figure 1–12, the composition is expressed in terms of the mole fraction of the *more* volatile component. Assume that a binary system with an overall composition of z exists in the vapor phase state as represented by point *A*. If the pressure on the system is increased, no phase change occurs until the dew point, *B*, is reached at pressure P_1. At this dew-point pressure, an infinitesimal amount of liquid forms whose composition is given by x_1. The composition of the vapor still is equal to the original composition z. As the

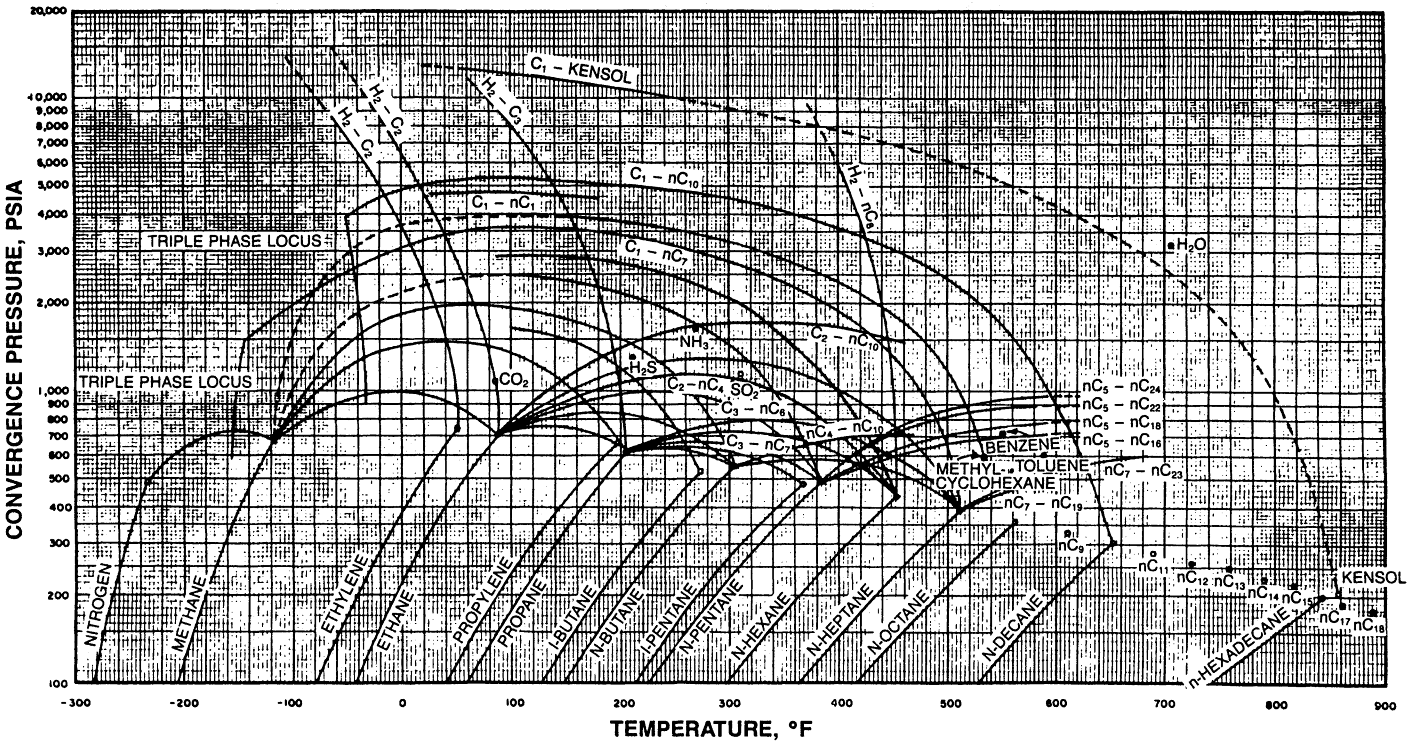


FIGURE 1–10 *Convergence pressures for binary systems.*

Source: GPSA Engineering Data Book, 10th ed. Tulsa, OK: Gas Processors Suppliers Association, 1987. Courtesy of the Gas Processors Suppliers Association.

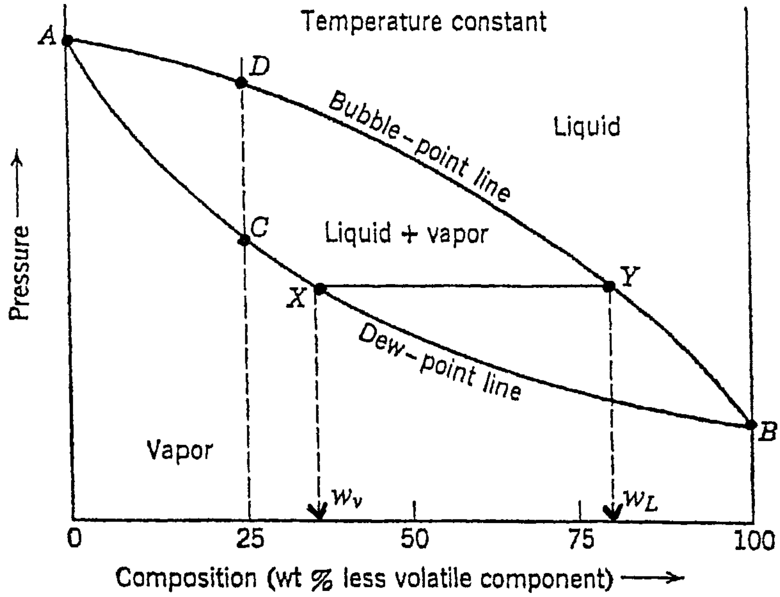


FIGURE 1–11 *Typical pressure/composition diagram for a two-component system. Composition expressed in terms of weight percent of the less volatile component.*

pressure is increased, more liquid forms and the compositions of the coexisting liquid and vapor are given by projecting the ends of the straight, horizontal line through the two-phase region of the composition axis. For example, at p_2, both liquid and vapor are present and the compositions are given by x_2 and y_2. At pressure p_3, the bubble point, C, is reached. The composition of the liquid is equal to the original composition z with an infinitesimal amount of vapor still present at the bubble point with a composition given by y_3.

As indicated already, the extremities of a horizontal line through the two-phase region represent the compositions of coexisting phases. Burcik (1957) points out that the *composition* and the *amount* of a each phase present in a two-phase system are of practical interest and use in reservoir engineering calculations. At the dew point, for example, only an infinitesimal amount of liquid is present, but it consists of finite mole fractions of the two components. An equation for the relative *amounts* of liquid and vapor in a two-phase system may be derived as follows:

Let

n = total number of moles in the binary system
n_L = number of moles of liquid
n_v = number of moles of vapor
z = mole fraction of the more volatile component in the system
x = mole fraction of the more volatile component in the liquid phase
y = mole fraction of the more volatile component in the vapor phase

By definition,

$n = n_L + n_v$
nz = moles of the more volatile component in the system

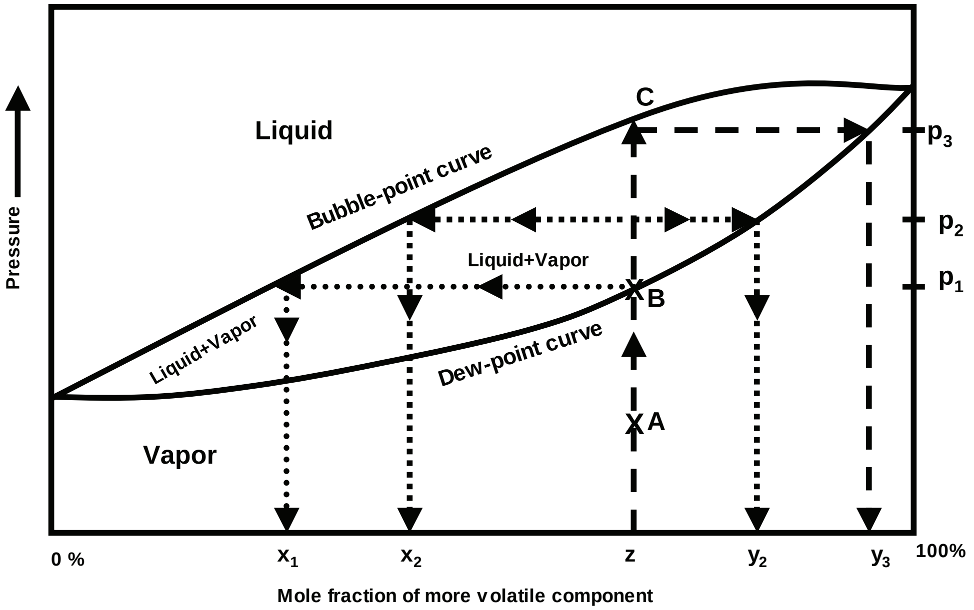


FIGURE 1–12 *Pressure/composition diagram illustrating isothermal compression through the two-phase region.*

$n_L x$ = moles of the more volatile component in the liquid
$n_v y$ = moles of the more volatile component in the vapor

A material balance on the more volatile component gives

$$nz = n_L x + n_v y \tag{1–13}$$

and

$$n_L = n - n_v$$

Combining these two expressions gives

$$nz = (n - n_v)x + n_v y$$

and rearranging one obtains

$$\frac{n_v}{n} = \frac{z - x}{y - x} \tag{1–14}$$

Similarly, if n_v is eliminated in equation (1–13) instead of n_L, we obtain

$$\frac{n_L}{n} = \frac{z - y}{x - y} \tag{1–15}$$

The geometrical interpretation of equations (1–14) and (1–15) is shown in Figure 1–13, which indicates that these equations can be written in terms of the two segments of the horizontal line *AC*. Since $z - x$ = the length of segment *AB*, and $y - x$ = the total length of horizontal line *AC*, equation (1–14) becomes

$$\frac{n_v}{n} = \frac{z - x}{y - x} = \frac{AB}{AC} \tag{1–16}$$

Similarly, equation (1–15) becomes

$$\frac{n_L}{n} = \frac{BC}{AC} \tag{1–17}$$

Equation (1–16) suggests that the ratio of the number of moles of vapor to the total number of moles in the system is equivalent to the length of the line segment *AB* that connects the overall composition to the liquid composition divided by the total length psia. This rule is known as the *inverse lever rule*. Similarly, the ratio of number of moles of liquid to the total number of moles in the system is proportional to the distance from the overall composition to the vapor composition *BC* divided by the total length *AC*. It should be pointed out that the straight line that connects the liquid composition with the vapor composition, that is, line *AC*, is called the *tie line*. Note that results would have been the same if the mole fraction of the less volatile component had been plotted on the phase diagram instead of the mole fraction of the more volatile component.

EXAMPLE 1–7

A system is composed of 3 moles of isobutene and 1 mole of n-heptanes. The system is separated at a fixed temperature and pressure and the liquid and vapor phases recovered. The mole fraction of isobutene in the recovered liquid and vapor are 0.370 and 0.965, respectively. Calculate the number of moles of liquid n_l and vapor n_v recovered.

SOLUTION

Step 1 Given $x = 0.370$, $y = 0.965$, and $n = 4$, calculate the overall mole fraction of isobutane in the system:

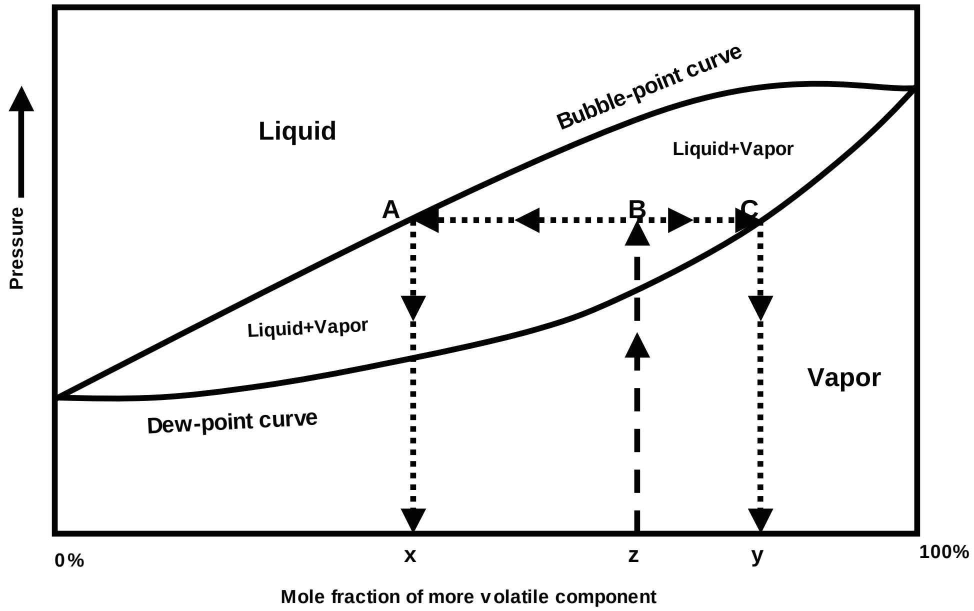


FIGURE 1–13 *Geometrical interpretation of equations for the amount of liquid and vapor in the two-phase region.*

$$z = \frac{3}{4} = 0.750$$

Step 2 Solve for the number of moles of the vapor phase by applying equation (1–14):

$$n_v = n\left(\frac{z-x}{y-x}\right) = 4\left(\frac{0.750-0.370}{0.965-0.375}\right) = 2.56 \text{ moles of vapor}$$

Step 3 Determine the quantity of liquid:

$$n_L = n - n_v = 4 - 2.56 = 1.44 \text{ moles of liquid}$$

The quantity of n_L also could be obtained by substitution in equation (1–15):

$$n_L = n\left(\frac{z-y}{x-y}\right) = 4\left(\frac{0.750-0.965}{0.375-0.965}\right) = 1.44$$

If the composition is expressed in weight fraction instead of mole fraction, similar expressions to those expressed by equations (1–14) and (1–15) can be derived in terms of weights of liquid and vapor. Let

m_t = total mass (weight) of the system
m_L = total mass (weight) of the liquid
m_v = total mass (weight) of the vapor
w_o = *weight fraction* of the more volatile component in the original system
w_L = weight fraction of the more volatile component in the liquid
w_v = weight fraction of the more volatile component in the vapor

A material balance on the more volatile component leads to the following equations:

$$\frac{m_v}{m_t} = \frac{w_o - w_L}{w_v - w_L}$$

$$\frac{m_L}{m_t} = \frac{w_o - w_v}{w_L - w_v}$$

Three-Component Systems

The phase behavior of mixtures containing three components (ternary systems) is conveniently represented in a triangular diagram, such as that shown in Figure 1–14. Such diagrams are based on the property of equilateral triangles that the sum of the perpendicular distances from any point to each side of the diagram is a constant and equal to the length on any of the sides. Thus, the composition x_i of the ternary system as represented by point *A* in the interior of the triangle of Figure 1–14 is

Component 1 $x_1 = \frac{L_1}{L_T}$

Component 2 $x_2 = \frac{L_2}{L_T}$

Component 3 $x_3 = \frac{L_3}{L_T}$

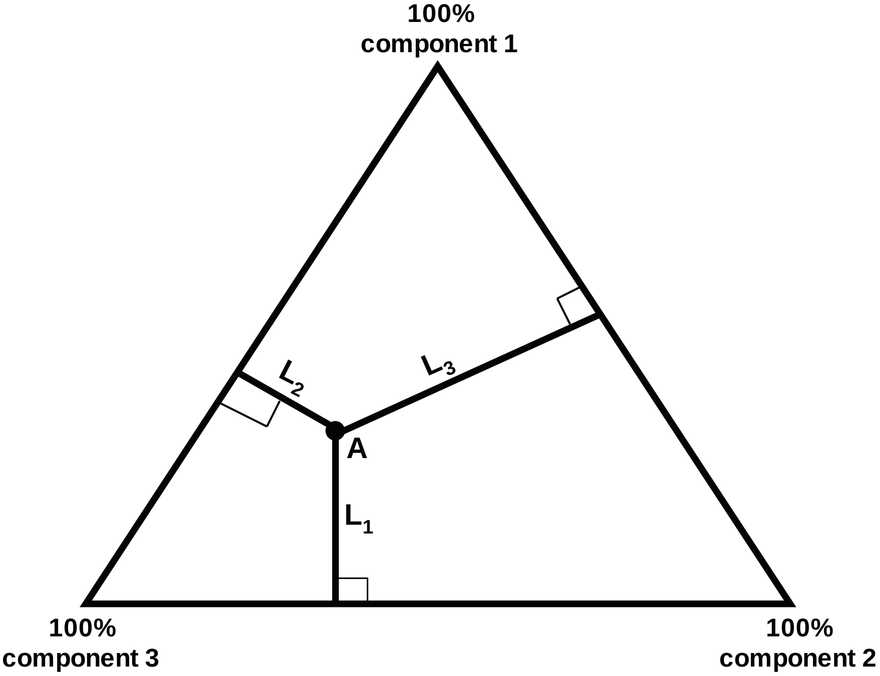


FIGURE 1–14 *Properties of the three-component diagram.*

where

$$L_T = L_1 + L_2 + L_3$$

Typical features of a ternary phase diagram for a system that exists in the two-phase region at fixed pressure and temperature are shown in Figure 1–15. Any mixture with an overall composition that lies inside the binodal curve (phase envelope) will split into liquid and vapor phases. The line that connects the composition of liquid and vapor phases that are in equilibrium is called the *tie line*. Any other mixture with an overall composition that lies on that tie line will split into the same liquid and vapor compositions. Only the amounts of liquid and gas change as the overall mixture composition changes from the liquid side (bubble-point curve) on the binodal curve to the vapor side (dew-point curve). If the mole fractions of component *i* in the liquid, vapor, and overall mixture are x_i, y_i, and z_i, the fraction of the total number of moles in the liquid phase n_l is given by

$$n_l = \frac{y_i - z_i}{y_i - x_i}$$

This expression is another *lever rule*, similar to that described for binary diagrams. The liquid and vapor portions of the binodal curve (phase envelope) meet at the plait point (critical point), where the liquid and vapor phases are identical.

Multicomponent Systems

The phase behavior of multicomponent hydrocarbon systems in the two-phase region, that is, the liquid-vapor region, is very similar to that of binary systems. However, as the

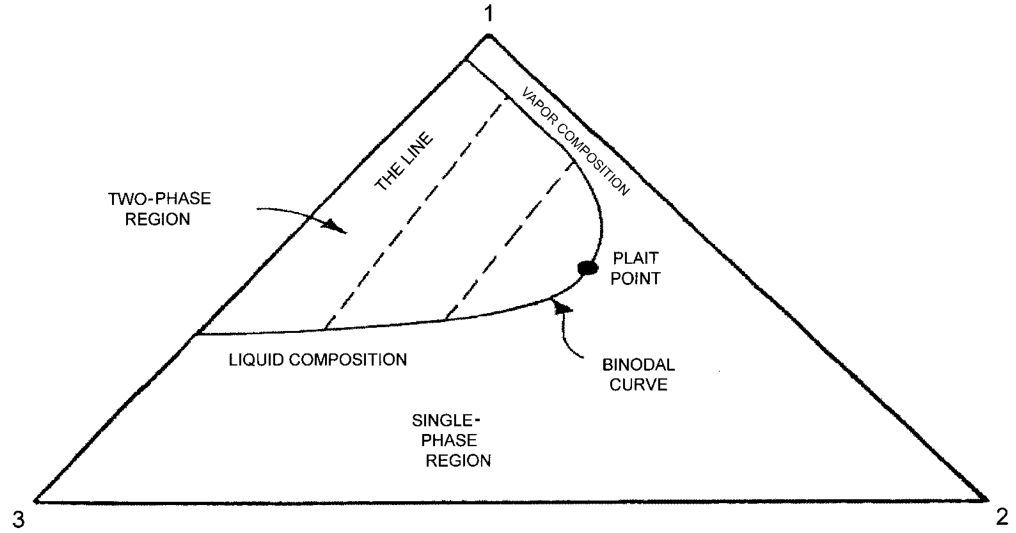


FIGURE 1–15 *Three-component phase diagram at a constant temperature and pressure for a system that forms a liquid and a vapor.*

system becomes more complex with a greater number of different components, the pressure and temperature ranges in which two phases lie increase significantly.

The conditions under which these phases exist are a matter of considerable practical importance. The experimental or the mathematical determinations of these conditions are conveniently expressed in different types of diagrams, commonly called *phase diagrams*. One such diagram is called the *pressure-temperature diagram*.

Figure 1–16 shows a typical pressure/temperature diagram (p/T diagram) of a multicomponent system with a specific overall composition. Although a different hydrocarbon system would have a different phase diagram, the general configuration is similar.

These multicomponent p/T diagrams are essentially used to classify reservoirs, specify the naturally occurring hydrocarbon systems, and describe the phase behavior of the reservoir fluid.

To fully understand the significance of the p/T diagrams, it is necessary to identify and define the following key points on the p/T diagram:

- *Cricondentherm* (T_{ct}) The cricondentherm is the maximum temperature above which liquid cannot be formed regardless of pressure (point *E*). The corresponding pressure is termed the *cricondentherm pressure*, p_{ct}.
- *Cricondenbar* (p_{cb}) The cricondenbar is the maximum pressure above which no gas can be formed regardless of temperature (point *D*). The corresponding temperature is called the *cricondenbar temperature*, T_{cb}.
- *Critical point* The critical point for a multicomponent mixture is referred to as the state of pressure and temperature at which all intensive properties of the gas and liquid phases are equal (point *C*). At the critical point, the corresponding pressure and temperature are called the *critical pressure*, p_c, and *critical temperature*, T_c, of the mixture.

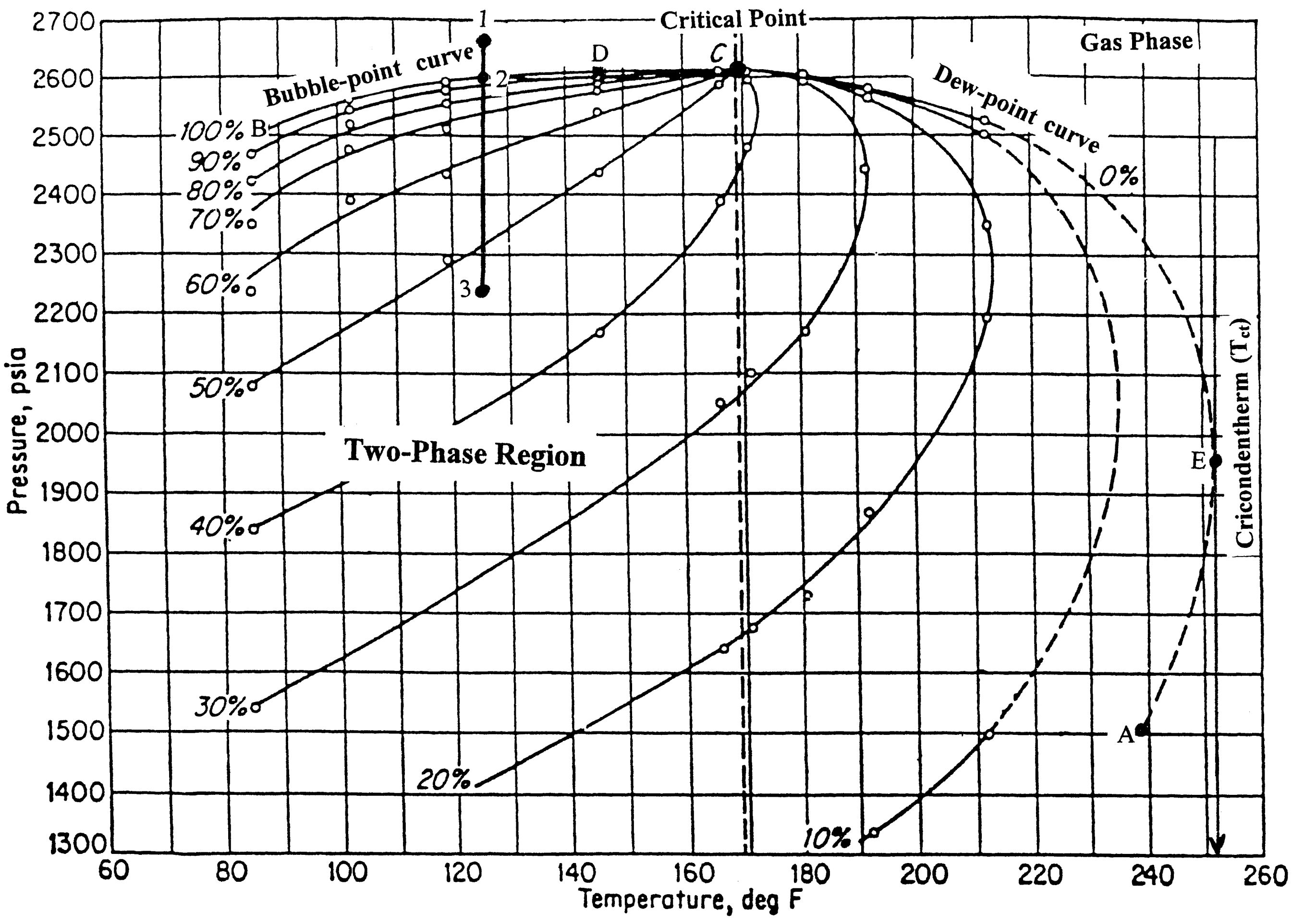


FIGURE 1–16 *Typical* p/T *diagram for a multicomponent system.*

- *Phase envelope (two-phase region)* The region enclosed by the bubble-point curve and the dew-point curve (line *BCA*), where gas and liquid coexist in equilibrium, is identified as the phase envelope of the hydrocarbon system.
- *Quality lines* The dashed lines within the phase diagram are called *quality lines*. They describe the pressure and temperature conditions for equal volumes of liquids. Note that the quality lines converge at the critical point (point *C*).
- *Bubble-point curve* The bubble-point curve (line *BC*) is defined as the line separating the liquid phase region from the two-phase region.
- *Dew-point curve* The dew-point curve (line *AC*) is defined as the line separating the vapor phase region from the two-phase region.

Classification of Reservoirs and Reservoir Fluids

Petroleum reservoirs are broadly classified as oil or gas reservoirs. These broad classifications are further subdivided depending on

1. The composition of the reservoir hydrocarbon mixture.
2. Initial reservoir pressure and temperature.
3. Pressure and temperature of the surface production.
4. Location of the reservoir temperature with respect to the critical temperature and the cricondentherm.

In general, reservoirs are conveniently classified on the basis of the location of the point representing the initial reservoir pressure p_i and temperature T with respect to the p/T diagram of the reservoir fluid. Accordingly, reservoirs can be classified into basically two types:

- *Oil reservoirs* If the reservoir temperature, T, is less than the critical temperature, T_c, of the reservoir fluid, the reservoir is classified as an oil reservoir.
- *Gas reservoirs* If the reservoir temperature is greater than the critical temperature of the hydrocarbon fluid, the reservoir is considered a gas reservoir.

Oil Reservoirs

Depending on initial reservoir pressure, p_i, oil reservoirs can be subclassified into the following categories:

1. *Undersaturated oil reservoir* If the initial reservoir pressure, p_i (as represented by point 1 on Figure 1–16), is greater than the bubble-point pressure, p_b, of the reservoir fluid, the reservoir is an undersaturated oil reservoir.
2. *Saturated oil reservoir* When the initial reservoir pressure is equal to the bubble-point pressure of the reservoir fluid, as shown on Figure 1–16 by point 2, the reservoir is a saturated oil reservoir.

3. *Gas-cap reservoir* If the initial reservoir pressure is below the bubble-point pressure of the reservoir fluid, as indicated by point 3 on Figure 1–16, the reservoir is a gas-cap or two-phase reservoir, in which an oil phase underlies the gas or vapor phase.

Crude oils cover a wide range in physical properties and chemical compositions, and it is often important to be able to group them into broad categories of related oils. In general, crude oils are commonly classified into the following types:

- Ordinary black oil.
- Low-shrinkage crude oil.
- High-shrinkage (volatile) crude oil.
- Near-critical crude oil.

This classification essentially is based on the properties exhibited by the crude oil, including:

- Physical properties, such as API gravity of the stock-tank liquid.
- Composition.
- Initial producing gas/oil ratio (GOR).
- Appearance, such as color of the stock-tank liquid.
- Pressure-temperature phase diagram.

Three of the above properties generally are available: initial GOR, API gravity, and color of the separated liquid.

The initial producing GOR perhaps is the most important indicator of fluid type. Color has not been a reliable means of differentiating clearly between gas condensates and volatile oils, but in general, dark colors indicate the presence of heavy hydrocarbons. No sharp dividing lines separate these categories of hydrocarbon systems, only laboratory studies could provide the proper classification. In general, reservoir temperature and composition of the hydrocarbon system greatly influence the behavior of the system.

1. *Ordinary black oil* A typical p/T phase diagram for ordinary black oil is shown in Figure 1–17. Note that quality lines that are approximately equally spaced characterize this black oil phase diagram. Following the pressure reduction path, as indicated by the vertical line *EF* in Figure 1–17, the liquid shrinkage curve, shown in Figure 1–18, is prepared by plotting the liquid volume percent as a function of pressure. The liquid shrinkage curve approximates a straight line except at very low pressures. When produced, ordinary black oils usually yield gas/oil ratios between 200 and 700 scf/STB and oil gravities of 15 to 40 API. The stock-tank oil usually is brown to dark green in color.
2. *Low-shrinkage oil* A typical p/T phase diagram for low-shrinkage oil is shown in Figure 1–19. The diagram is characterized by quality lines that are closely spaced near the dew-point curve. The liquid shrinkage curve, given in Figure 1–20, shows the

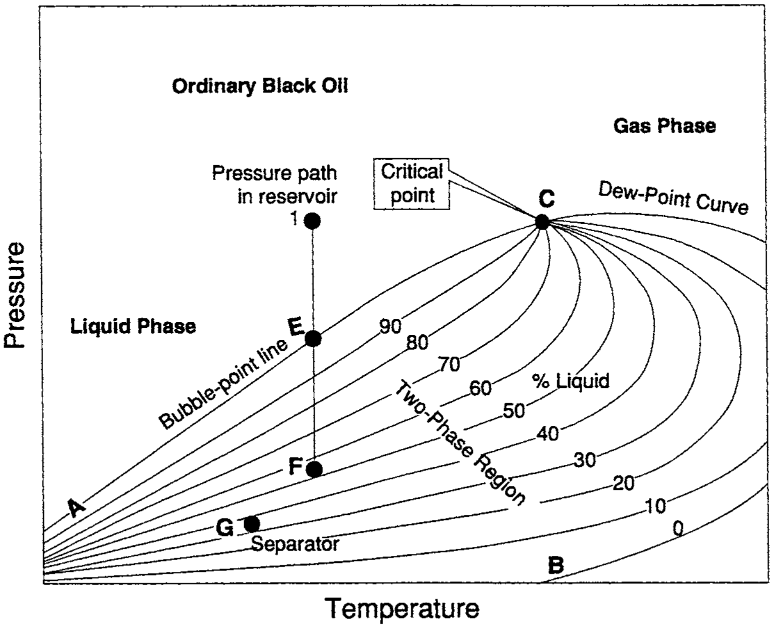


FIGURE 1–17 *Typical* p/T *diagram for ordinary black oil.*

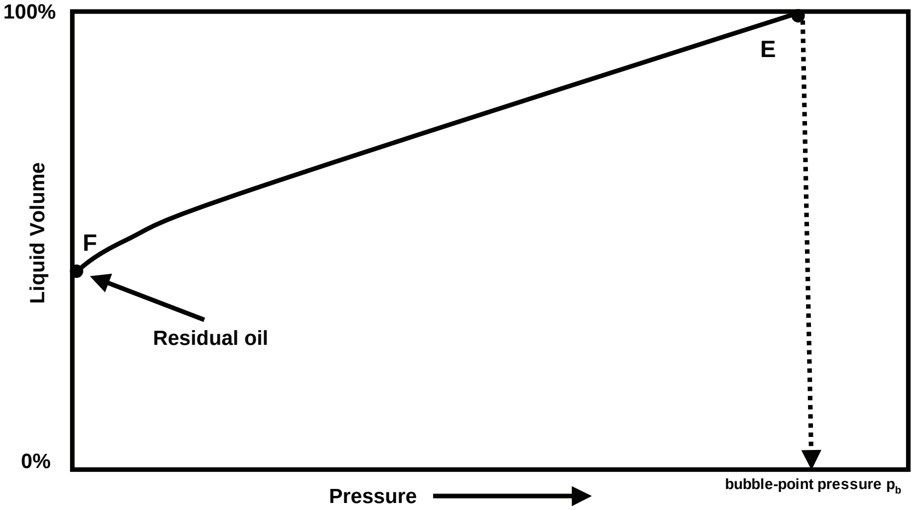


FIGURE 1-18 *Liquid shrinkage curve for black oil.*

shrinkage characteristics of this category of crude oils. The other associated properties of this type of crude oil are

- Oil formation volume factor less than 1.2 bbl/STB.
- Gas-oil ratio less than 200 scf/STB.
- Oil gravity less than 35° API.
- Black or deeply colored.

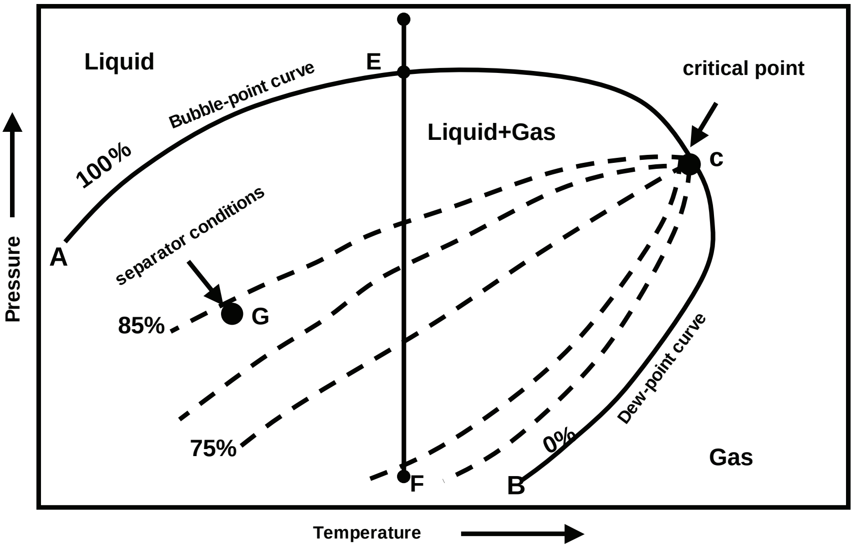


FIGURE 1–19 *Typical phase diagram for low-shrinkage oil.*

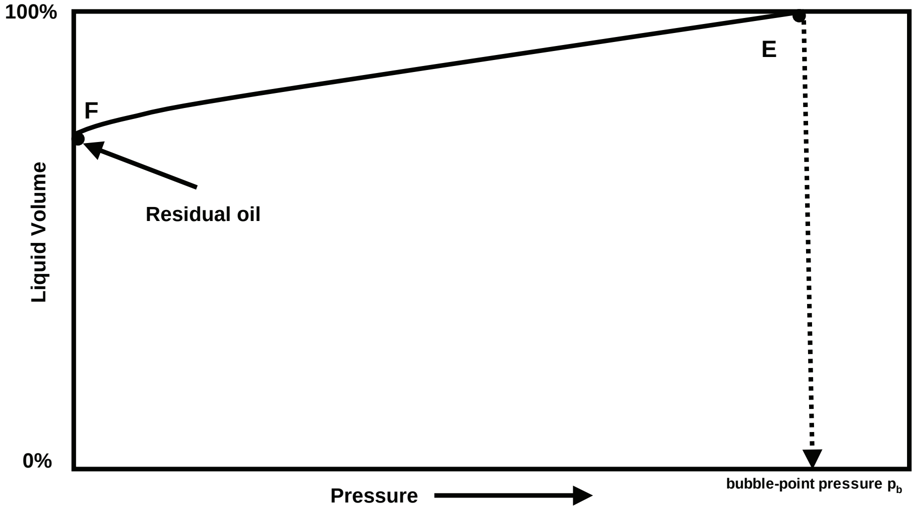


FIGURE 1–20 *Oil shrinkage curve for low-shrinkage oil.*

- Substantial liquid recovery at separator conditions as indicated by point *G* on the 85% quality line of Figure 1–19.

3. *Volatile crude oil* The phase diagram for a volatile (high-shrinkage) crude oil is given in Figure 1–21. Note that the quality lines are close together near the bubble point, and at lower pressures, they are more widely spaced. This type of crude oil is commonly characterized by a high liquid shrinkage immediately below the bubble point, shown in Figure 1–22. The other characteristic properties of this oil include:

- Oil formation volume factor greater than 1.5 bbl/STB.

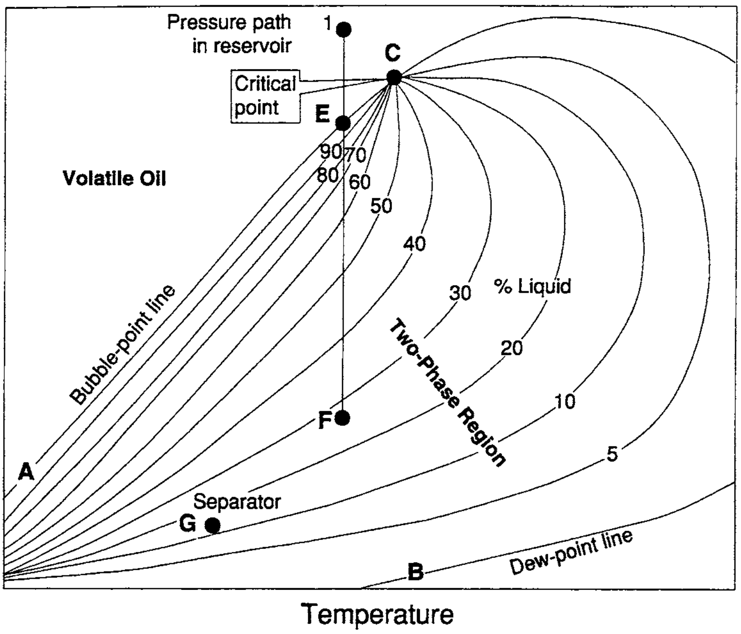


FIGURE 1–21 *Typical* p/T *diagram for a volatile crude oil.*

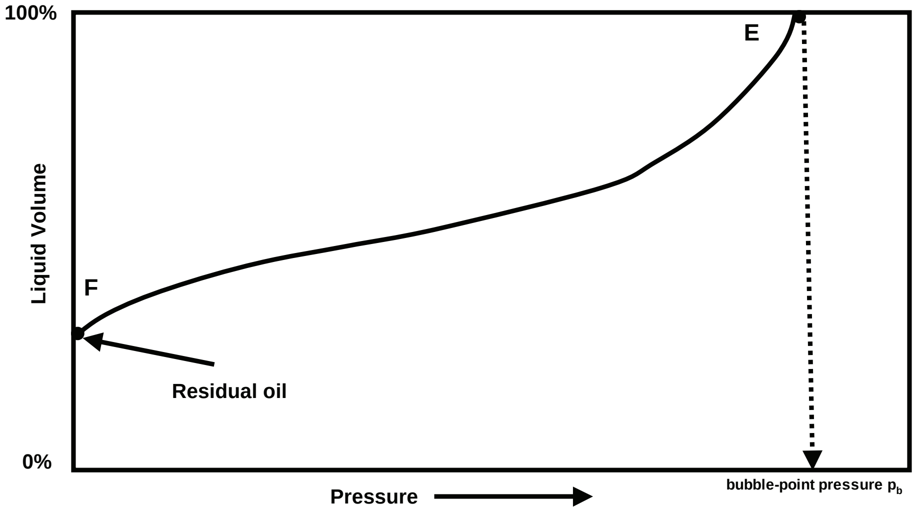


FIGURE 1–22 *Typical liquid shrinkage curve for a volatile crude oil.*

- Gas-oil ratios between 2000 and 3000 scf/STB.
- Oil gravities between 45° and 55° API.
- Lower liquid recovery of separator conditions, as indicated by point *G* on Figure 1–19.
- Greenish to orange in color.

Solution gas released from a volatile oil contains significant quantities of stock-tank liquid (condensate) when the solution gas is produced at the surface. Solution gas from black oils usually is considered "dry," yielding insignificant stock-tank liquid when produced to surface conditions. For engineering calculations, the liquid content of released solution gas perhaps is the most important distinction between volatile oils and black oils. Another characteristic of volatile oil reservoirs is that the API gravity of the stock tank liquid increases in the later life of the reservoirs.

4. *Near-critical crude oil* If the reservoir temperature, T, is near the critical temperature, T_c, of the hydrocarbon system, as shown in Figure 1–21, the hydrocarbon mixture is identified as a near-critical crude oil. Because all the quality lines converge at the critical point, an isothermal pressure drop (as shown by the vertical line *EF* in Figure 1–23) may shrink the crude oil from 100% of the hydrocarbon pore volume at the bubble point to 55% or less at a pressure 10 to 50 psi below the bubble point. The shrinkage characteristic behavior of the near-critical crude oil is shown in Figure 1–24. This high shrinkage creates high gas saturation in the pore space and because of the gas-oil relative permeability characteristics of most reservoir rocks; free gas achieves high mobility almost immediately below the bubble-point pressure.

   The near-critical crude oil is characterized by a high GOR, in excess of 3000 scf/STB, with an oil formation volume factor of 2.0 bbl/STB or higher. The compositions of near-critical oils usually are characterized by 12.5 to 20 mol% heptanes-plus, 35% or more of ethane through hexanes, and the remainder methane. It should be pointed out that near-critical oil systems essentially are considered the borderline to very rich gas condensates on the phase diagram.

Figure 1–25 compares the characteristic shape of the liquid shrinkage curve for each crude oil type.

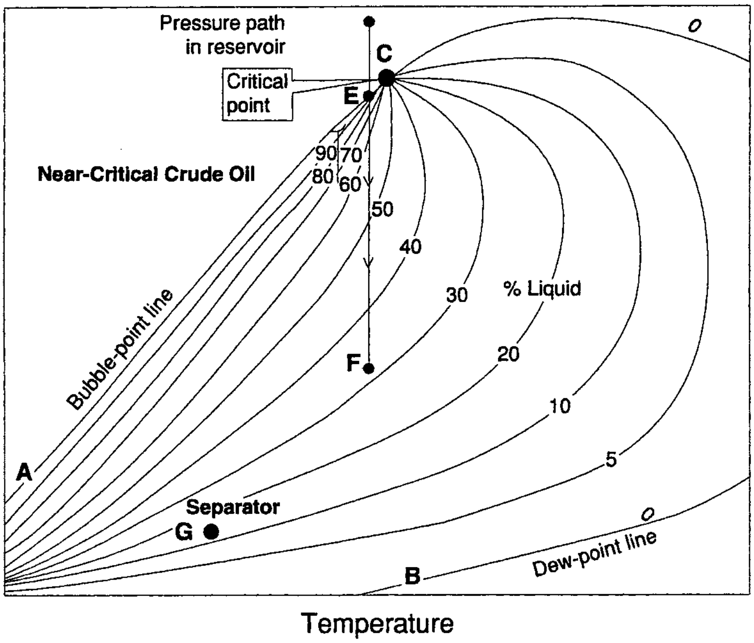


FIGURE 1–23 *Phase diagram for a near-critical crude oil.*

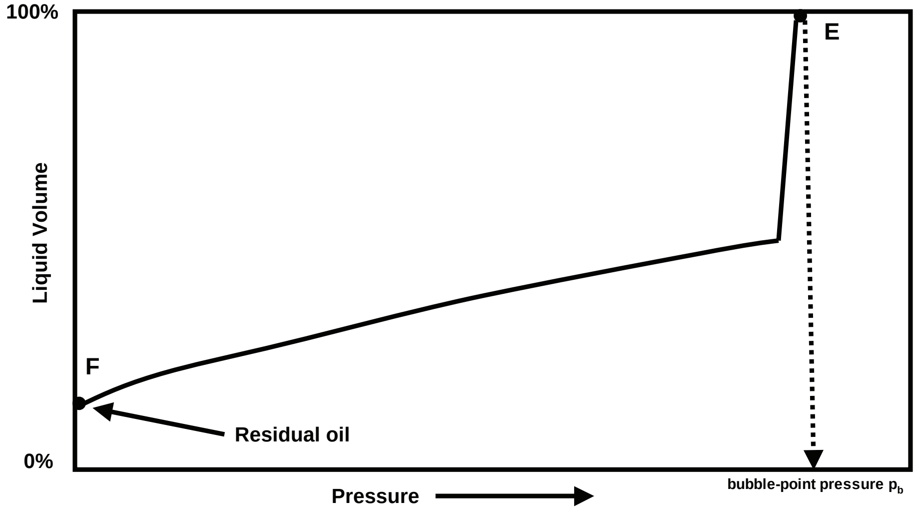


FIGURE 1–24 *Typical liquid shrinkage curve for a near-critical crude oil.*

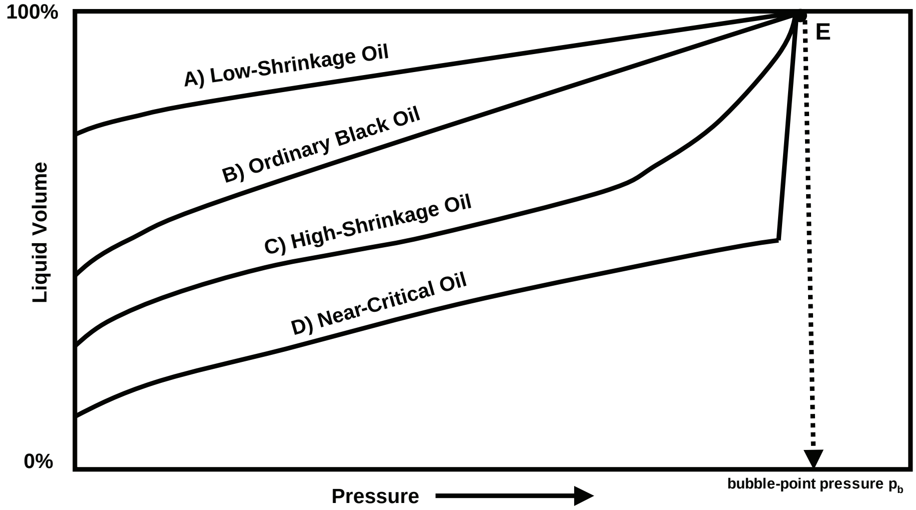


FIGURE 1–25 *Liquid shrinkage curves for crude oil systems.*

Gas Reservoirs

In general, if the reservoir temperature is above the critical temperature of the hydrocarbon system, the reservoir is classified as a natural gas reservoir. Natural gases can be categorized on the basis of their phase diagram and the prevailing reservoir condition into four categories:

1. Retrograde gas reservoirs.
2. Near-critical gas-condensate reservoirs.
3. Wet gas reservoirs.
4. Dry gas reservoirs.

In some cases, when condensate (stock-tank liquid) is recovered from a surface process facility, the reservoir is mistakenly classified as a retrograde gas reservoir. Strictly speaking, the definition of a retrograde gas reservoir depends only on reservoir temperature.

Retrograde Gas Reservoirs

If the reservoir temperature, T, lies between the critical temperature, T_c, and cricondentherm, T_{ct}, of the reservoir fluid, the reservoir is classified as a retrograde gas-condensate reservoir. This category of gas reservoir has a unique type of hydrocarbon accumulation, in that the special thermodynamic behavior of the reservoir fluid is the controlling factor in the development and the depletion process of the reservoir. When the pressure is decreased on these mixtures, instead of expanding (if a gas) or vaporizing (if a liquid) as might be expected, they vaporize instead of condensing.

Consider that the initial condition of a retrograde gas reservoir is represented by point 1 on the pressure-temperature phase diagram of Figure 1–26. Because the reservoir pressure is above the upper dew-point pressure, the hydrocarbon system exists as a single phase (i.e., vapor phase) in the reservoir. As the reservoir pressure declines isothermally during production from the initial pressure (point 1) to the upper dew-point pressure (point 2), the attraction between the molecules of the light and heavy components move further apart. As this occurs, attraction between the heavy component molecules becomes more effective, therefore, liquid begins to condense. This retrograde condensation process continues with decreasing pressure until the liquid dropout reaches its maximum at point 3. Further reduction in pressure permits the heavy molecules to commence the normal vaporization process. This is the process whereby fewer gas molecules strike the liquid

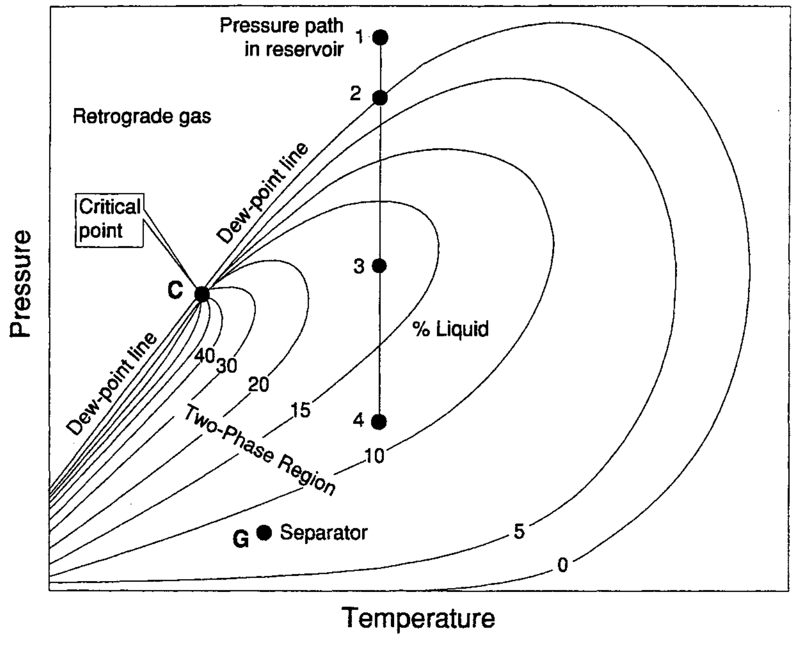


FIGURE 1–26 *Typical phase diagram of a retrograde system.*

surface and more molecules leave than enter the liquid phase. The vaporization process continues until the reservoir pressure reaches the lower dew-point pressure. This means that all the liquid that formed must vaporize because the system essentially is all vapor at the lower dew point.

Figure 1–27 shows a typical liquid shrinkage volume curve for a relatively rich condensate system. The curve is commonly called the *liquid dropout curve*. The maximum liquid dropout (LDO) is 26.5%, which occurs when the reservoir pressure drops from a dew-point pressure of 5900 psi to 2800 psi. In most gas-condensate reservoirs, the condensed liquid volume seldom exceeds more than 15–19% of the pore volume. This liquid saturation is not large enough to allow any liquid flow. It should be recognized, however,

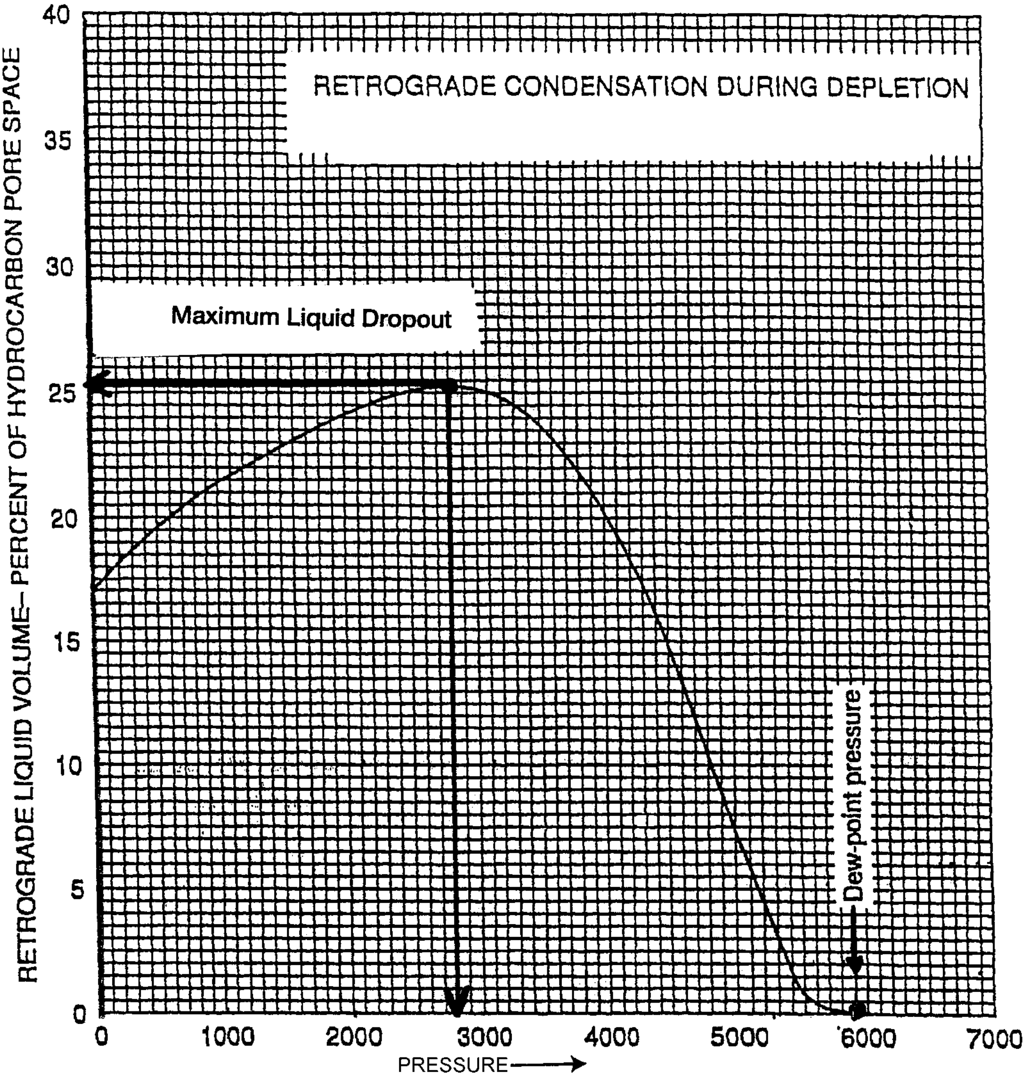


FIGURE 1–27 *Typical liquid dropout curve.*

that around the well bore, where the pressure drop is high, enough liquid dropout might accumulate to give two-phase flow of gas and retrograde liquid.

The associated physical characteristics of this category are

- Gas-oil ratios between 8000 and 70,000 scf/STB. Generally, the gas-oil ratio for a condensate system increases with time due to the liquid dropout and the loss of heavy components in the liquid.
- Condensate gravity above 50° API.
- Stock-tank liquid is usually water-white or slightly colored.

It should be pointed out that the gas that comes out of the solution from a volatile oil and remains in the reservoir typically is classified a retrograde gas and exhibits the retrograde condensate with pressure declines.

There is a fairly sharp dividing line between oils and condensates from a compositional standpoint. Reservoir fluids that contain heptanes and are in concentration of more than 12.5 mol% almost always are in the liquid phase in the reservoir. Oils have been observed with heptanes and heavier concentrations as low as 10% and condensates as high as 15.5%. These cases are rare, however, and usually have very high tank liquid gravities.

Near-Critical Gas-Condensate Reservoirs

If the reservoir temperature is near the critical temperature, as shown in Figure 1–28, the hydrocarbon mixture is classified as a near-critical gas condensate. The volumetric behavior of this category of natural gas is described through the isothermal pressure declines, as shown by the vertical line 1–3 in Figure 1–28 and the corresponding liquid dropout curve of Figure 1–29. Because all the quality lines converge at the critical point, a rapid liquid buildup immediately occurs below the dew point (Figure 1–29) as the pressure is reduced to point 2.

This behavior can be justified by the fact that several quality lines are crossed very rapidly by the isothermal reduction in pressure. At the point where the liquid ceases to build up and begins to shrink again, the reservoir goes from the retrograde region to a normal vaporization region.

Wet Gas Reservoirs

A typical phase diagram of a wet gas is shown in Figure 1–30, where the reservoir temperature is above the cricondentherm of the hydrocarbon mixture. Because the reservoir temperature exceeds the cricondentherm of the hydrocarbon system, the reservoir fluid always remains in the vapor phase region as the reservoir is depleted isothermally, along the vertical line *AB*. However, as the produced gas flows to the surface, the pressure and temperature of the gas decline. If the gas enters the two-phase region, a liquid phase condenses out of the gas and is produced from the surface separators. This is caused by a sufficient decrease in the kinetic energy of heavy molecules with temperature drop and their subsequent change to liquid through the attractive forces between molecules.

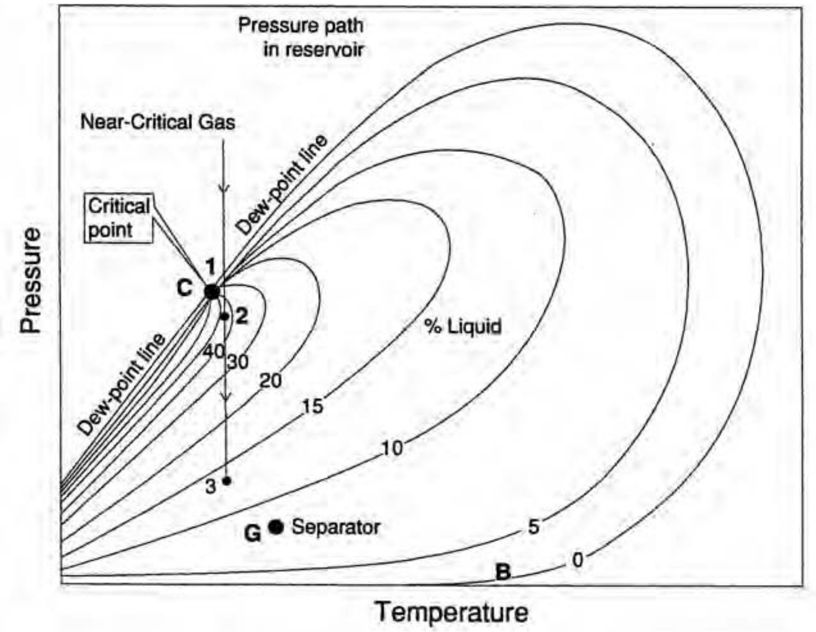


FIGURE 1–28 *Typical phase diagram for a near-critical gas condensate reservoir.*

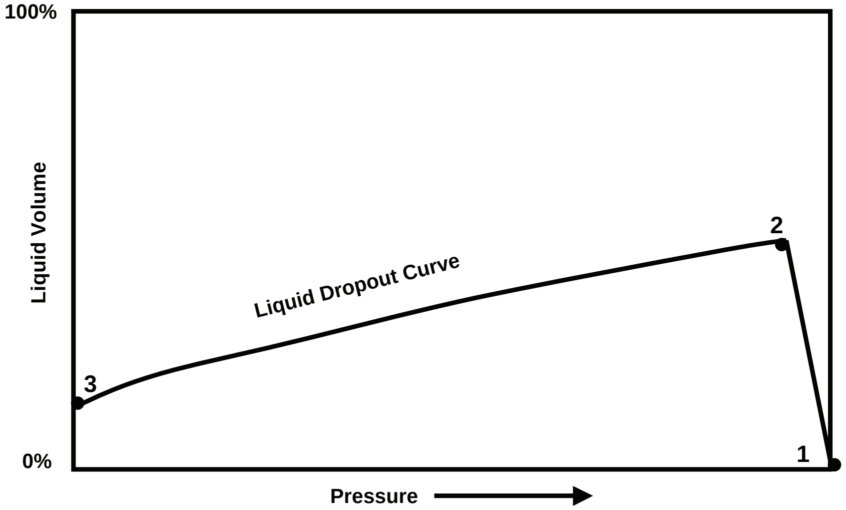


FIGURE 1–29 *Liquid shrinkage curve for a near-critical gas condensate system.*

Wet gas reservoirs are characterized by the following properties:

- Gas oil ratios between 60,000 and 100,000 scf/STB.
- Stock-tank oil gravity above 60° API.
- Liquid is water-white in color.
- Separator conditions (i.e., separator pressure and temperature) lie within the two-phase region.

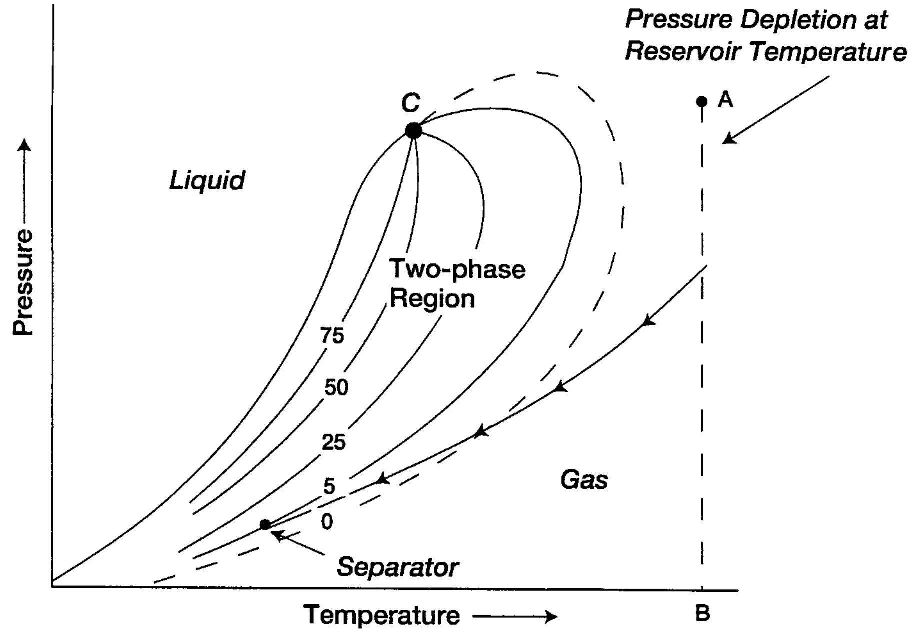


FIGURE 1–30 *Phase diagram for a wet gas.*
Source: After N. J. Clark, *Elements of Petroleum Reservoirs,* 2nd ed. Tulsa, OK: Society of Petroleum Engineers, 1969.

Dry Gas Reservoirs

The hydrocarbon mixture exists as a gas both in the reservoir and the surface facilities. The only liquid associated with the gas from a dry gas reservoir is water. Figure 1–31 is a phase diagram of a dry gas reservoir. Usually, a system that has a gas/oil ratio greater than 100,000 scf/STB is considered to be a dry gas. The kinetic energy of the mixture is so high and attraction between molecules so small that none of them coalesce to a liquid at stock-tank conditions of temperature and pressure.

It should be pointed out that the listed classifications of hydrocarbon fluids might be also characterized by the initial composition of the system. McCain (1994) suggests that the heavy components in the hydrocarbon mixtures have the strongest effect on fluid characteristics. The ternary diagram shown in Figure 1–32 with equilateral triangles can be conveniently used to roughly define the compositional boundaries that separate different types of hydrocarbon systems.

Fluid samples obtained from a new field discovery may be instrumental in defining the existence of a two-phase, that is, gas-cap, system with an overlying gas cap or underlying oil rim. As the compositions of the gas and oil zones are completely different from each other, both systems may be represented separately by individual phase diagrams, which bear little relation to each other or to the composite. The oil zone will be at its bubble point and produced as a saturated oil reservoir but modified by the presence of the gas cap. Depending on the composition and phase diagram of the gas, the gas-cap gas may be a retrograde gas cap, as shown in Figure 1–33, or dry or wet, as shown in Figure 1–34. Therefore, a discovery well drilled through a saturated reservoir fluid usually requires further field delineation

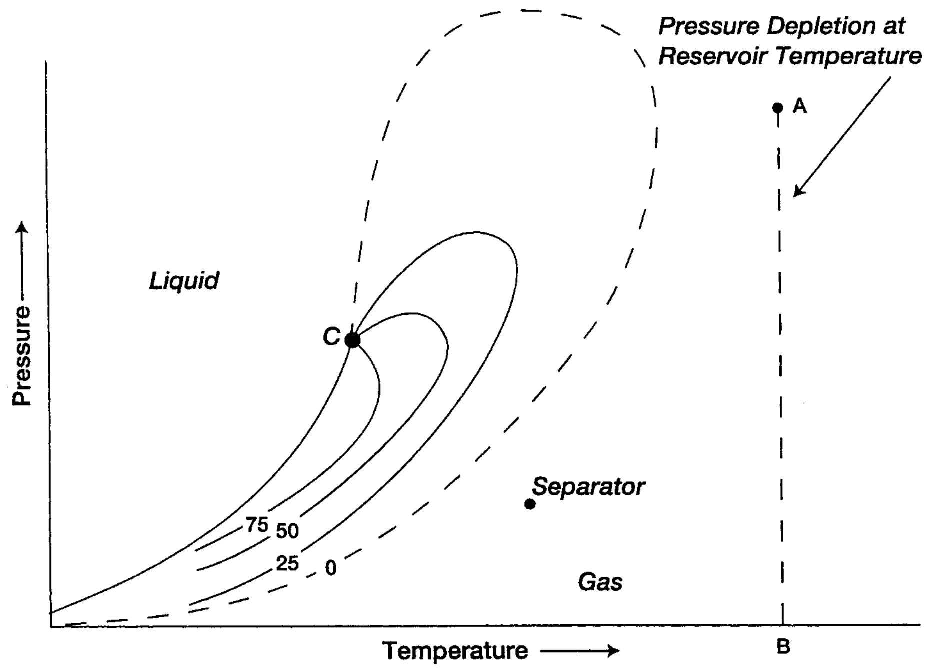


FIGURE 1–31 *Phase diagram for a dry gas.*
Source: After N. J. Clark, *Elements of Petroleum Reservoirs*, 2nd ed. Tulsa, OK: Society of Petroleum Engineers, 1969.

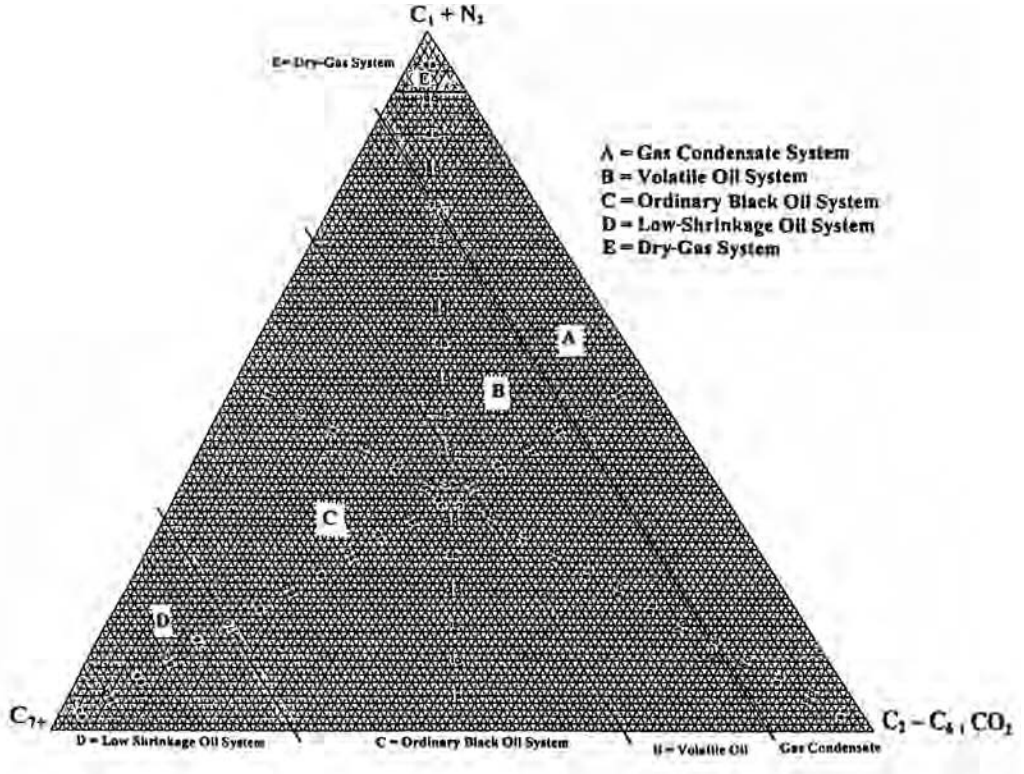


FIGURE 1–32 *Composition of various reservoir fluid systems.*

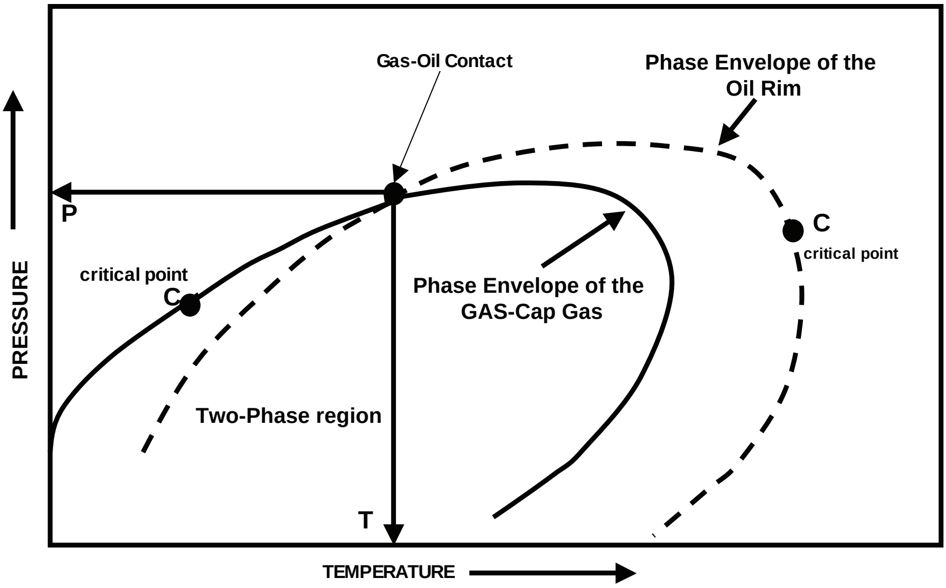


FIGURE 1–33 *Retrograde gas-cap reservoir.*

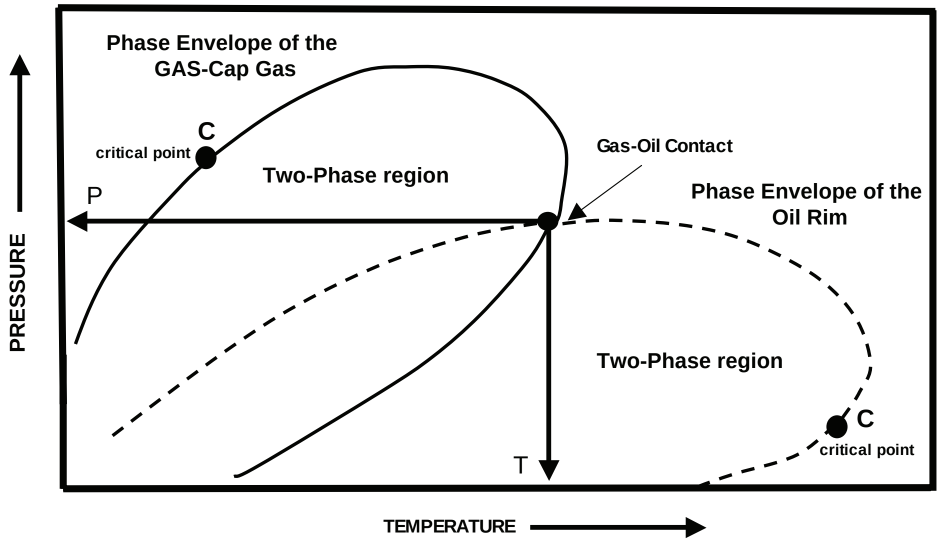


FIGURE 1–34 *Dry gas-cap reservoir.*

to substantiate the presence of a second equilibrium phase above (i.e., gas cap) or below (i.e., oil rim) the tested well. This may entail running a repeat-formation-tester tool to determine fluid-pressure gradient as a function of depth; or a new well may be required updip or downdip to that of the discovery well.

When several samples are collected at various depths, they exhibit PVT properties as a function of the depth expressed graphically to locate the gas-oil contact (GOC). The variations of PVT properties can be expressed graphically in terms of the compositional changes of C_1 and C_{7+} with depth and in terms of well-bore and stock-tank densities with depth, as shown in Figures 1–35 through 1–37.

Defining the fluid contacts, that is, GOC and water-oil contact (WOC), are extremely important when determining the hydrocarbon initially in place and planning field development. The uncertainty in the location of the fluid contacts can have a significant impact on the reserves estimate. Contacts can be determined by

1. Electrical logs, such as resistively tools.
2. Pressure measurements, such as a repeat formation tester (RFT) or a modular formation dynamic tester (MDT).
3. Possibly by interpreting seismic data.

Normally, unless a well penetrates a fluid contact directly, there remains doubt as to its locations. The RFT is a proprietary name used by Schlumberger for an open-hole logging tool used to establish vertical pressure distribution in the reservoir (i.e., it provides a pressure-depth profile in the reservoir) and to obtain fluid samples. At the appraisal stage of a new field, the RFT survey provides the best-quality pressure data and routinely is run to establish fluid contacts. The surveys are usually straightforward to interpret compared to the drill-stem tests (DSTs), because no complex buildup analysis is required to determine the reservoir pressure nor are any extensive depth corrections to be applied, since the gauge depth is practically coincidental with that of the RFT probe.

The RFT tool is fitted with a pressure transducer and positioned across the target zone. The device is placed against the side of the bore hole by a packer. A probe that consists of two pretest chambers, each fitted with a piston, is pushed against the formation and

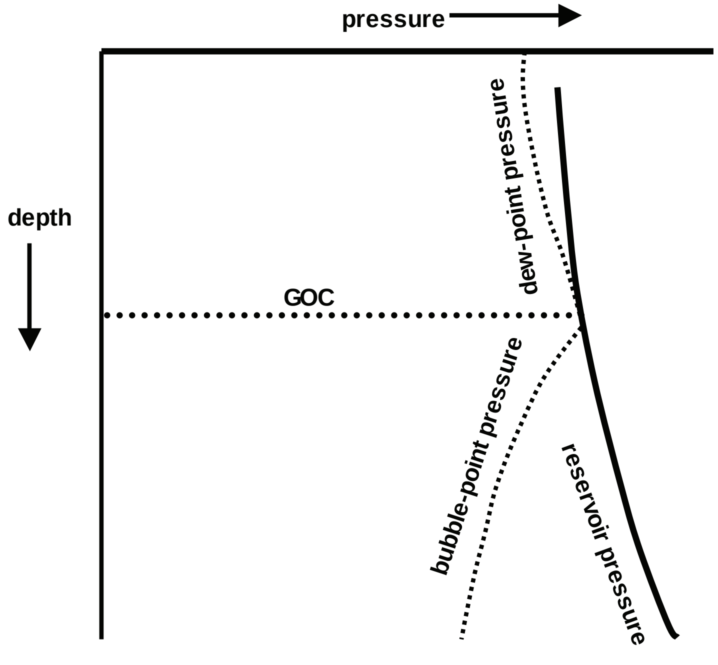


FIGURE 1–35 *Determination of GOC from pressure gradients.*

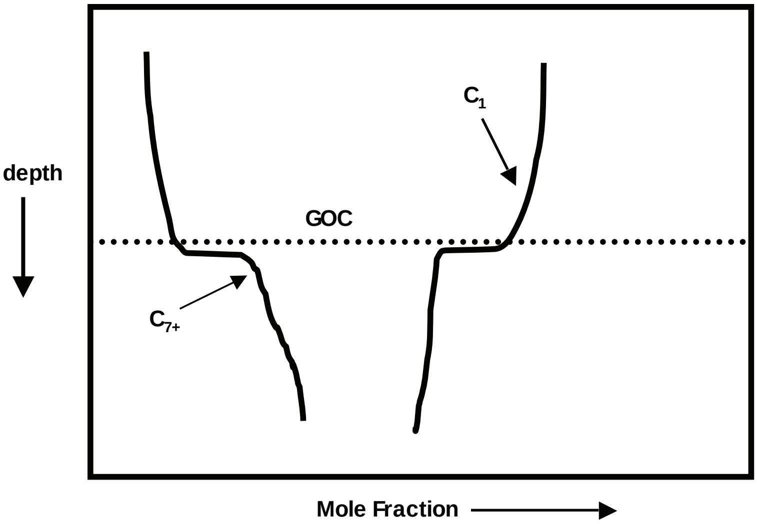


FIGURE 1–36 *Compositional changes of C_1 and C_{7+} with depth.*

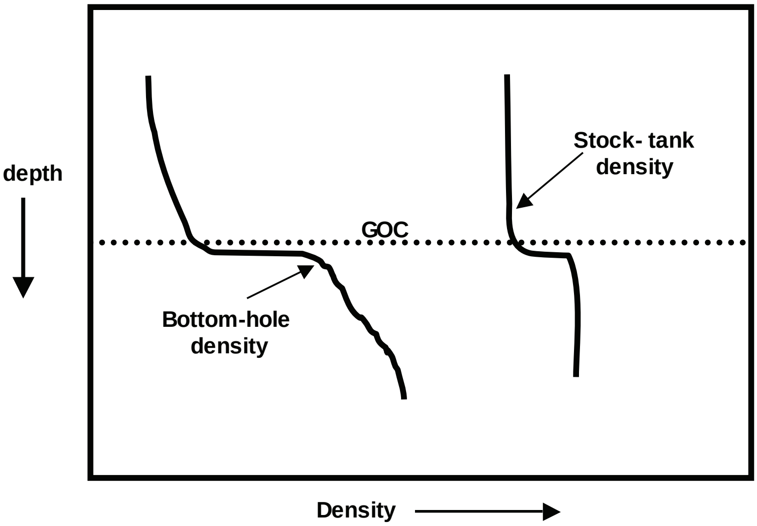


FIGURE 1–37 *Variation of well-bore and stock-tank density with depth.*

through the mud cake. A pressure drawdown is created at the probe by withdrawing the pistons in the pretest chambers. These two chambers operate in series: The first piston is withdrawn slowly (taking about 4 seconds to withdraw 10 cm^3 of fluid); the second piston is withdrawn at a faster rate, 5 seconds for 10 cm^3. Before the tool is set against the formation, the pressure transducer records the mud pressure at the target depth.

As the first pretest chamber is filled (slowly) with fluid; the first main pressure drop Δp_1 is observed, followed by Δp_2 as the second pretest chamber is filled. The tighter the formation, the larger Δp_1 and Δp_2 are. The recording, therefore, gives a qualitative indication of the permeability of the reservoir. Because the flow rate and pressure drop are known, the actual formation permeability can be calculated, and this is done by the CSU (the computer in the logging unit). Caution should be attached to the permeability values, since a very small part of the reservoir is being tested and the analysis assumes a particular flow regime, which may not be representative in some cases. The reliability of the values should be regarded as indicating the order of magnitude of the permeability.

Once both drawdowns have occurred, fluid withdrawal stops and the formation pressure is allowed to recover. This recovery is recorded as the pressure buildup, which should stabilize at the true formation fluid pressure at the depth. Note that the drawdown pressure drops, Δp_1 and Δp_2, are relative to the final pressure buildup and not to the initial pressure, which was the mud pressure. The rate of pressure buildup can be used to estimate permeability; the test therefore gives three permeability estimates at the same sample point.

A tight formation leads to very large pressure drawdowns and a slow buildup. If the pressure has not built up within 4–5 minutes, the pressure test usually is abandoned for fear of the tool becoming stuck. The tool is retracted and the process repeated at a new depth. Once the tool is unset, the pressure reading should return to the same mud pressure as prior to setting. This is used as a quality control check on gauge drift. There is no limit as to the number of depths at which pressure samples may be taken.

If a fluid sample is required, this can be done by diverting the fluid flow during sampling to sample chambers in the tool.

It should be pointed out that, when plotting the pressure against depth, the unit of pressures must be kept consistent, that is, either in absolute pressure (psia) or gauge pressure (psig). The depth must be the true vertical depth, preferably below the subsurface datum depth.

The basic principle of pressure versus depth plotting is illustrated in Figure 1–38. This illustration shows two wells:

- Well 1 penetrates the gas cap with a recorded gas pressure of p_g and a measured gas density of ρ_g.
- Well 2 penetrates the oil zone with a recorded oil pressure of p_o and oil density of ρ_o.

The gas, oil, and water gradients can be calculated from:

$$\frac{dp_g}{dh}=\frac{\rho_g}{144}=\gamma_g$$

$$\frac{dp_o}{dh}=\frac{\rho_o}{144}=\gamma_o$$

$$\frac{dp_w}{dh}=\frac{\rho_w}{144}=\gamma_w$$

where

dp/dh = fluid gradient, psi/ft
γ_g = gas gradient, psi/ft
γ_o = oil gradient, psi/ft
γ_w = water gradient, psi/ft
ρ_g = gas density, lb/ft^3

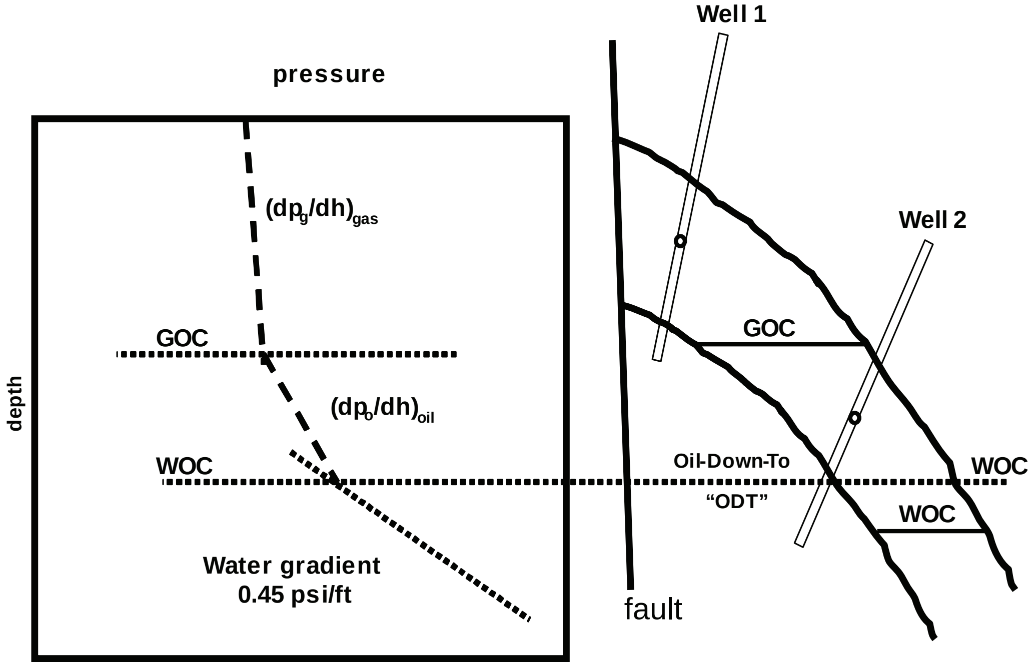


FIGURE 1–38 *Pressure gradient versus depth.*

ρ_o = oil density, lb/ft^3
ρ_w = water density, lb/ft^3

As shown in Figure 1–38, the intersection of the gas and oil gradient lines locates the position of the gas-oil contact. Note that the oil can be seen only down to a level termed the oil-down-to (ODT) level. The level is assigned to the oil-water contact unless a well is drilled further downdip to locate the WOC.

Figure 1–39 shows another case where a well penetrated an oil column. Oil can be seen down to the ODT level. However, a gas cap may exist. If the pressure of the oil is recorded as p_o and the bubble-point pressure is measured as p_b at this specific depth, the gas-oil contact can be determined from

$$\Delta D = \frac{p_o - p_b}{\left(\frac{dp}{dh}\right)_{\text{oil}}} = \frac{p_o - p_b}{\gamma_o} \tag{1–18}$$

If the calculated value of ΔD locates the GOC within the reservoir, then there is a possibility that a gas cap exists, but this is not certain. Equation (1–18) assumes that the PVT properties, including the bubble-point pressure, do not vary with depth. The only way to be certain that a gas cap exists is to drill a crestal well.

A similar scenario that can be encountered is illustrated Figure 1–40. Here, a discovery well penetrates a gas column with gas as seen down to the gas-down-to (GDT) level, which allows the possibility of a downdip oil rim. If the field operator feels that an oil rim

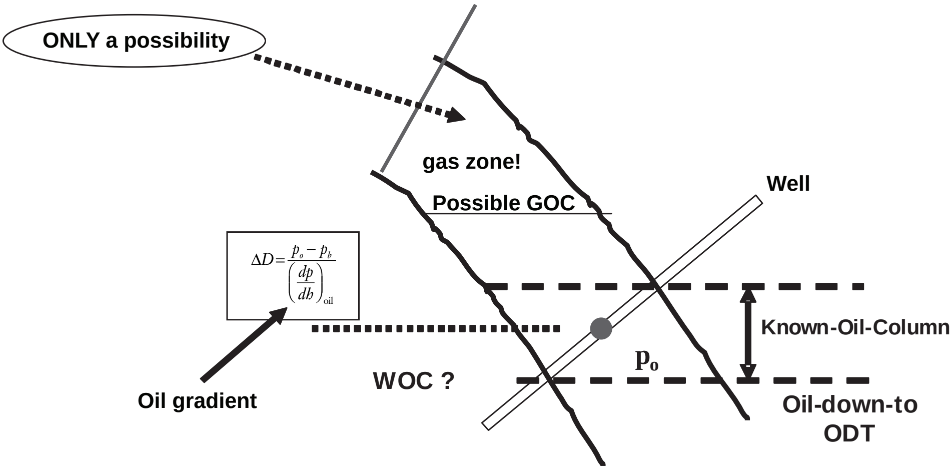


FIGURE 1–39 *A well in the oil rim. A discovery well penetrates an oil column. What is the possibility of a gas cap updip?*

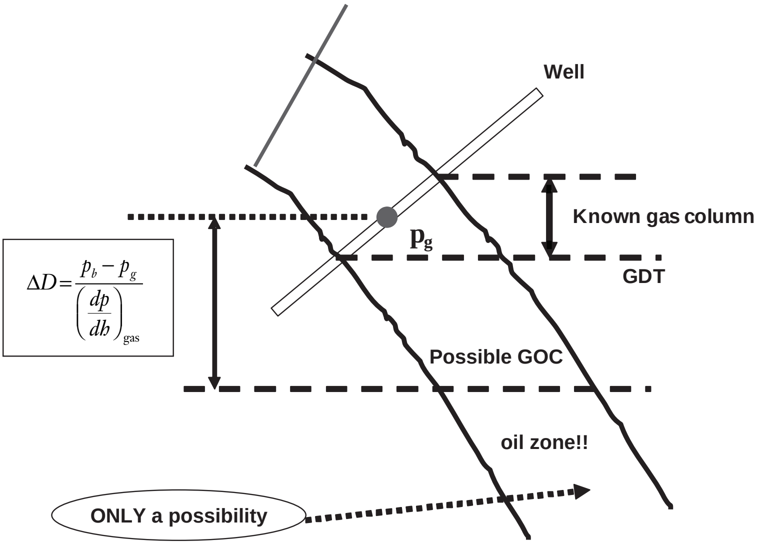


FIGURE 1–40 *A discovery well penetrates a gas column. What is the possibility of an oil rim?*

exists, based on similarity with other fields in the area, the distance to GOC can be estimated from

$$\Delta D = \frac{p_b - p_g}{\left(\frac{dp}{dh}\right)_{gas}} = \frac{p_b - p_g}{\gamma_g}$$

Figure 1-41 shows a case where two wells are drilled: The first well is in the gas column and the second penetrates the water zone. Of course, only two possibilities could exist:

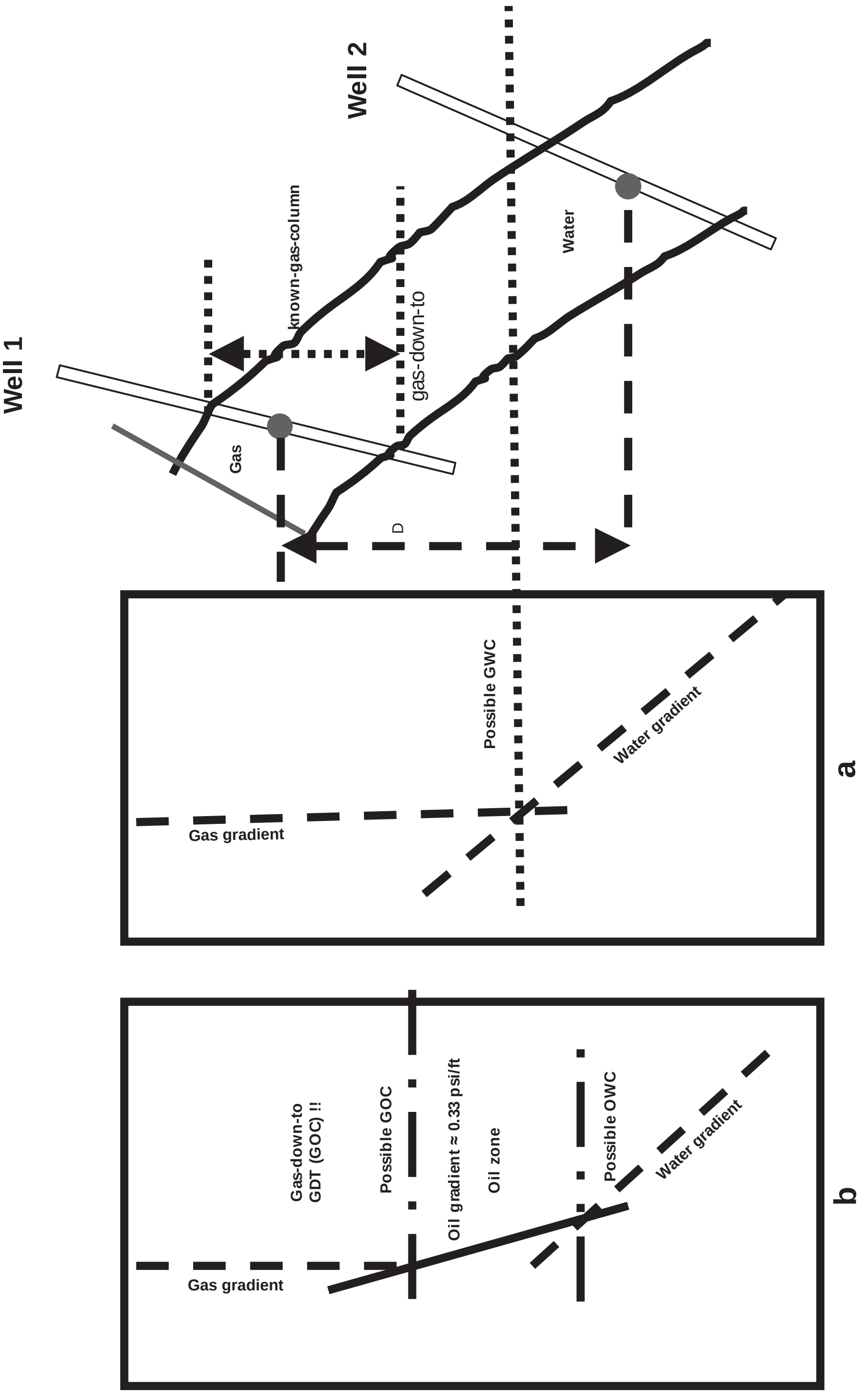


FIGURE 1–41 *Two discovery wells.*

1. The first possibility is shown in Figure 1–41(a), which suggests a known gas column with an underlying water zone. Also, the gas-water contact (GWC) has not been established. A "possible" GWC can be calculated from the following relationship:

$$D_1 = \frac{p_g - \left[p_w - D\left(\frac{dp}{dh}\right)_{\text{water}} \right]}{\left(\frac{dp}{dh}\right)_{\text{water}} - \left(\frac{dp}{dh}\right)_{\text{gas}}} = \frac{p_g - \left[p_w - D\gamma_{\text{water}} \right]}{\gamma_{\text{water}} - \gamma_{\text{gas}}}$$

   where

   γ = fluid gradient, psi/ft that is, $\rho/144$
   ρ = fluid density, lb/ft^3
   D_1 = vertical distance between gas well and GWC, ft
   D = vertical distance between the two wells
   $dp/dh = \gamma$ = fluid gradient, psi/ft

2. The second possibility is shown in Figure 1–41(a), where a possible oil zone exists between the two wells. Assuming a range of oil gradients, such as 0.28–0.38 psi/ft, the maximum possible oil thickness can be estimated graphically as shown in Figure 1–41(b), by drawing a line originating at the GDT level with a slope in the range of 0.28–0.38 psi/ft to intersect with the water gradient line.

If the bubble point pressure can be assumed, the maximum oil column thickness can be estimated, as shown in Figure 1–42, from the following expression:

$$\Delta D_2 = \frac{\Delta D\left(\frac{dp_w}{dh}\right) - (p_w - p_b) - (p_b - p_g)\frac{dp_w / dh}{dp_g / dh}}{\frac{dp_w}{dh} - \frac{dp_o}{dh}} = \frac{\Delta D\gamma_w - (p_w - p_b) - (p_b - p_g)\frac{\gamma_w}{\gamma_g}}{\gamma_w - \gamma_o}$$

where

ΔD_2 = maximum possible oil column thickness, ft
ΔD = vertical distance between the two wells, ft
dp/dh = fluid pressure gradient, psi/ft

EXAMPLE 1–8

Figure 1–43 shows two wells. One penetrated the gas zone at 4950 ft true vertical depth (TVD) and the other in the water zone at 5150 ft. Pressures and PVT data follow:

p_g = 1745 psi
ρ_g = 14.4 lb/ft^3
p_w = 1808 psi
ρ_w = 57.6 lb/ft^3

A nearby field has a bubble-point pressure of 1750 psi and an oil density of 50.4 lb/ft^3 (ρ_o = 50.4 lb/ft^3). Calculate

1. Possible depth to GOC.

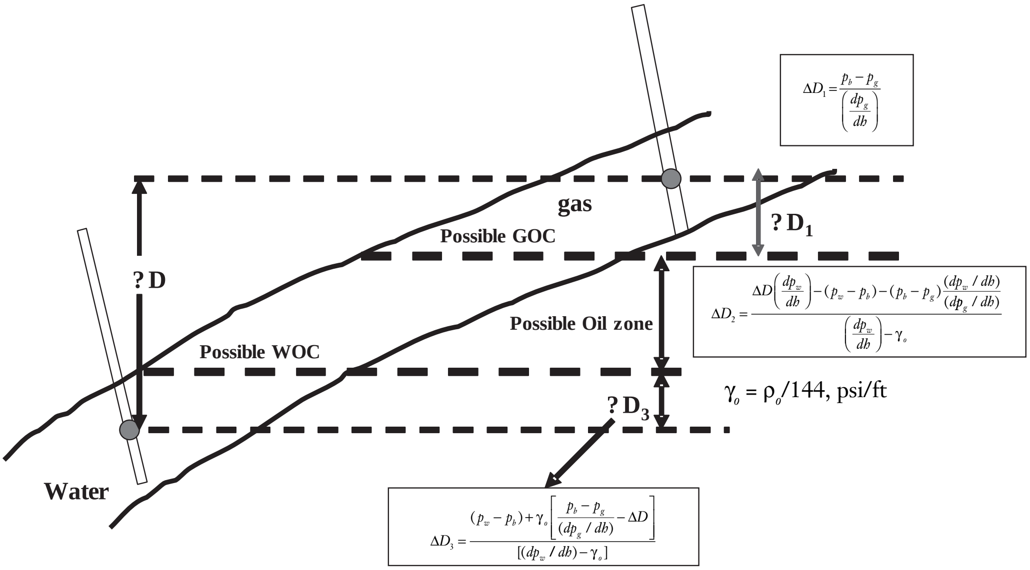


FIGURE 1–42 *Two discovery wells, maximum possible oil thickness.*

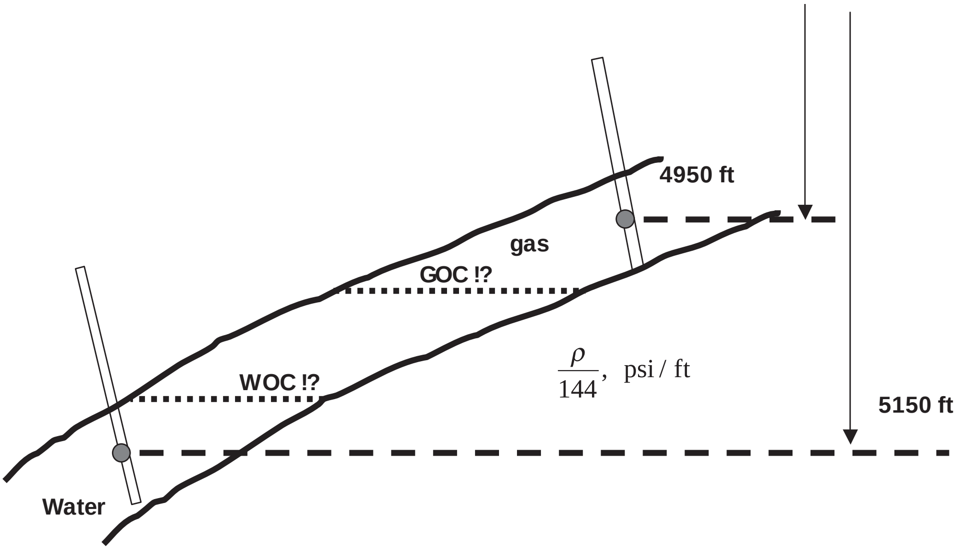


FIGURE 1–43 *Example 1–8.*

2. Maximum possible oil column thickness.
3. Possible depth to WOC.

SOLUTION

Step 1 Calculate the pressure gradient of each phase:

Gas phase $$\left(\frac{dp}{dh}\right)_{\text{gas}} = \frac{\rho_g}{144} = \frac{14.4}{144} = 0.1\,\text{psi/ft}$$

Oil phase $$\left(\frac{dp}{dh}\right)_{\text{oil}}=\frac{\rho_o}{144}=\frac{50.4}{144}=0.35\,\text{psi/ft}$$

Water phase $$\left(\frac{dp}{dh}\right)_{\text{water}}=\frac{\rho_w}{144}=\frac{57.6}{144}=0.4\,\text{psi/ft}$$

Step 2 Calculate the distance to the possible GOC:

$$\text{GOC}=4950+\frac{p_b-p_g}{dp_g\,/\,dh}=4595+\frac{1750-1745}{0.10}=5000\text{ ft}$$

Step 3 Calculate maximum oil rim thickness:

$$\Delta D_2=\frac{\Delta D\gamma_w-(p_w-p_b)-(p_b-p_g)\dfrac{\gamma_w}{\gamma_g}}{\gamma_w-\gamma_o}$$

$$\Delta D_2=\text{ maximum oil thickness}=\frac{200(0.4)-(1808-1750)-(1750-1745)\dfrac{(0.4)}{(0.1)}}{(0.4)-(0.35)}=40\text{ ft}$$

Step 4 Possible depth to WOC:

WOC = 5000 + 40 = 5040 ft

Phase Rule

It is appropriate at this stage to introduce and define the concept of the phase rule. Gibbs (1948 [1876]) derived a simple relationship between the number of phases, P, in equilibrium, the number of components, C, and the number of independent variables, F, that must be specified to describe the state of the system completely.

Gibbs proposed the following fundamental statement of the phase rule:

$$F=C-P+2 \tag{1–19}$$

where

F = number of variables required to determine the state of the system at equilibrium or number of degrees of freedom (such as pressure, temperature, density)
C = number of independent components
P = number of phases

A phase was defined as a homogeneous system of uniform physical and chemical compositions. The degrees of freedom, F, for a system include the intensive properties such as temperature, pressure, density, and composition (concentration) of phases. These independent variables must be specified to define the system completely. In a single component ($C = 1$), two-phase system ($P = 2$), there is *only* 1 degree of freedom ($F = 1 - 2 + 2 = 1$); therefore, only pressure or temperature needs to be specified to determine the thermodynamic state of the system.

The phase rule as described by equation (1–19) is useful in several ways. It indicates the maximum number of equilibrium phases that can coexist and the number of components present. It should be pointed out that the phase rule does not determine the nature, exact composition, or total quantity of the phases. Furthermore, it applies only to a system in stable equilibrium and does not determine the rate at which this equilibrium is attained.

The importance and the practical application of the phase rule are illustrated through the following examples.

EXAMPLE 1–9

For a single-component system, determine the number of degrees of freedom required for the system to exist in the single-phase region.

SOLUTION

Applying equation (1–19) gives $F = 1 - 1 + 2 = 2$. Two degrees of freedom must be specified for the system to exist in the single-phase region. These must be the pressure p and the temperature T.

EXAMPLE 1–10

What degrees of freedom are allowed for a two-component system in two phases?

SOLUTION

Since $C = 2$ and $P = 2$, applying equation (1–19) yields $F = 2 - 2 + 2 = 2$. The two degrees of freedom could be the system pressure p and the system temperature T, and the concentration (mole fraction), or some other combination of T, p, and composition .

EXAMPLE 1–11

For a three-component system, determine the number of degrees of freedom that must be specified for the system to exist in the one-phase region.

SOLUTION

Using the phase rule expression gives $F = 3 - 1 + 2 = 4$, four independent variables must be specified to fix the system. The variables could be the pressure, temperature, and mole fractions of two of the three components.

From the foregoing discussion it can be observed that hydrocarbon mixtures may exist in either the gas or liquid state, depending on the reservoir and operating conditions to which they are subjected. The qualitative concepts presented may be of aid in developing quantitative analyses. Empirical equations of state are commonly used as a quantitative tool in describing and classifying the hydrocarbon system. These equations of state require

- Detailed compositional analysis of the hydrocarbon system.
- Complete description of the physical and critical properties of the mixture of the individual components.

Problems

1. The following is a list of the compositional analysis of different hydrocarbon systems, with the compositions as expressed in terms of mol%. Classify each of these systems.