

2. PHASE BEHAVIOR

Petroleum reservoir fluids are composed mainly of hydrocarbon constituents. Water is also present in gas and oil reservoirs in an interstitial form. The influence of water on the phase behavior and properties of hydrocarbon fluids in most cases is of a minor consideration. The phase behavior of oil and gas, therefore, is generally treated independent of the water phase, unless water–hydrocarbon solid structures, known as hydrates, are formed.

The behavior of a hydrocarbon mixture at reservoir and surface conditions is determined by its chemical composition and the prevailing temperature and pressure. This behavior is of a prime consideration in the development and management of reservoirs, affecting all aspects of petroleum exploration and production. Although a reservoir fluid may be composed of many thousands of compounds, the phase behavior fundamentals can be explained by examining the behavior of pure and simple multicomponent mixtures. The behavior of all real reservoir fluids basically follows the same principle, but to facilitate the application of the technology in the industry, reservoir fluids have been classified into various groups such as the dry gas, wet gas, gas condensate, volatile oil and black oil.

2.1 RESERVOIR FLUID COMPOSITION

There are various hypotheses regarding the formation of petroleum from organic materials. These views suggest that the composition of a reservoir fluid depends on the depositional environment of the formation, its geological maturity, and the migration path from the source to trap rocks [1]. Reservoir gasses are mainly composed of hydrocarbon molecules of small and medium sizes and some light non–hydrocarbon compounds such as nitrogen and carbon dioxide, whereas oils are predominantly composed of heavier compounds.

Fluids advancing into a trapping reservoir may be of different compositions due to being generated at different times and environments. Hence, lateral and vertical compositional variations within a reservoir will be expected during the early reservoir life. Reservoir fluids are generally considered to have attained equilibrium at maturity due to molecular diffusion and mixing over geological times. However, there are ample evidences of reservoirs still maintaining significant compositional variations, particularly laterally as the diffusive mixing may require many tens of million years to eliminate compositional heterogeneities [2]. Furthermore, the pressure and the temperature increase with depth for a fluid column in a reservoir. This can also result in compositional grading with depth. For operational purposes, this behavior is of considerable interest for near critical fluids, and oils containing high concentrations of asphaltic material. Compositional grading and its estimation will be further discussed later.

The crude oil composition is of major consideration in petroleum refining. A number of comprehensive research projects sponsored by the American Petroleum Institute have investigated crude oil constituents and identified petroleum compounds. API–6 studied the composition of a single crude oil for 40 years. The Sulphur, nitrogen and organometallic compounds of crude oil samples were investigated in projects API–48, API–52 and API–56 respectively. API–60 studied petroleum heavy ends. Nelson (1958) [3] gives a review of petroleum chemistry and test methods used in the refining industry.

Highly detailed information on the constituents composing a reservoir fluid is not of very much use in exploration and production processes. Reservoir fluids are commonly identified by their constituents individually to pentanes, and heavier compounds are reported as groups composed mostly of components with equal number of carbons such as C₆, C₇, C₈ and C₉. All the compounds forming each

single carbon number group do not necessarily possess the same number of carbons as will be discussed later. The most common method of describing the heavy fraction is to lump all the compounds heavier than C6 and report it as C7+, or all heavier than C9 as C10+.

Hydrocarbon compounds can be expressed by the general formula of $C_nH_{2n+\xi}$ with some Sulphur, nitrogen, oxygen and minor metallic elements mostly present in heavy fractions. Hydrocarbon compounds are classified according to their structures, which determine the value of the major classes are paraffins (alkanes), olefins (alkenes), naphthenes, and aromatics. The paraffin series are composed of saturated hydrocarbon straight chains with $\xi=2$. Light paraffins in reservoir fluids are sometimes identified and reported as those with a single hydrocarbon chain, as normal, and others with branched chain hydrocarbons, as iso. The olefin series ($\xi=0$) have unsaturated straight chains and are not usually found in reservoir fluids due to their unstable nature. The naphthenes are cyclic compounds composed of saturated ring(s) with $\xi=0$. The aromatics ($\xi=-6$) are unsaturated cyclic compounds. Naphthenes and aromatics form a major part of C6–C11 groups and some of them such as methyl–cyclo–pentane, benzene, toluene and xylene are often individually identified in the extended analysis of reservoir fluids. For example, the structural formulas of the above groups of hydrocarbons with six carbons are shown in Fig. 2.1.

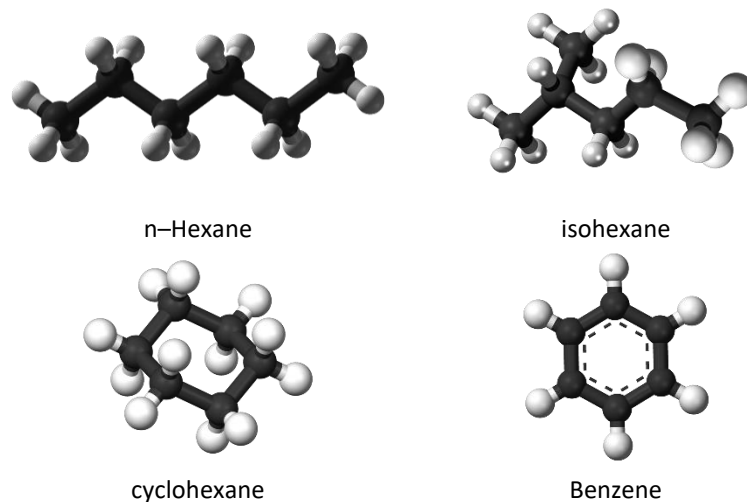


Fig. 2.1. Structural formula of various hydrocarbons with six carbons.

As reservoir hydrocarbon liquids may be composed of many thousand components, they cannot all be identified and measured. However, the concentration of hydrocarbon components belonging to the same structural class are occasionally measured and reported as groups, particularly for gas condensate fluids. The test to measure the concentration of Paraffins, Naphthenes, and Aromatics as groups is commonly referred to as the PNA test [23]. Further information on the structure of reservoir fluid compounds and their labelling according to the IUPAC system can be found in [5]. The compositional analysis of reservoir fluids and their characterization will be discussed later.

Nitrogen, oxygen and Sulphur are found in light and heavy fractions of reservoir fluids. Gas reservoirs containing predominantly N_2 , H_2S , or CO_2 have also been discovered. Polycyclic hydrocarbons with fused rings which are more abundant in heavier fractions may contain N, S, and O. These compounds such as carbides, carbenes, asphaltenes and resins are identified by their solubility, or lack of it, in different solvents [6]. The polar nature of these compounds can affect the properties of reservoir fluids, particularly the rock–fluid behavior, disproportionately higher than their concentrations [7]. These heavy compounds may be present in colloidal suspension in the reservoir oil and precipitate out of solution by changes in the pressure, temperature or compositions occurring during production.

2.2 PHASE BEHAVIOUR

Reservoir hydrocarbons exist as vapor, liquid or solid phases. A phase is defined as a part of a system which is physically distinct from other parts by definite boundaries. A reservoir oil (liquid phase) may form gas (vapor phase) during depletion. The evolved gas initially remains dispersed in the oil phase before forming large mobile clusters, but the mixture is considered as a two-phase system in both cases. The formation or disappearance of a phase, or variations in properties of a phase in a multi-phase system are rate phenomena. The subject of phase behavior, however, focuses only on the state of equilibrium, where no changes will occur with time if the system is left at the prevailing constant pressure and temperature. A system reaches equilibrium when it attains its minimum energy level, as will be discussed later. The assumption of equilibrium between fluid phases in contact in a reservoir, in most cases, is valid in engineering applications. Fluids at equilibrium are also referred to as saturated fluids.

The state of a phase is fully defined when its composition, temperature and pressure are specified. All the intensive properties for such a phase at the prevailing conditions are fixed and identifiable. The intensive properties are those which do not depend on the amount of material (contrary to the extensive properties), such as the density and the specific heat. The term property throughout this book refers to intensive properties. At equilibrium, a system may form of a number of co-existing phases, with all the fluid constituents present in all the equilibrated phases. The number of independent variables to define such a system is determined by the Gibbs phase rule described as follows.

A phase composed of N components is fully defined by its number of moles plus two thermodynamic functions, commonly temperature and pressure, that is, by $N+2$ variables. The intensive properties are, however, determined by only $N+1$ variables as the concentration of components are not all independent, but constrained by,

$$\sum_1^N x_i = 1 \quad (2.1)$$

where, x_i is the mole fraction of component i .

Thus, for a system with κ phases, the total number of variables are equal to $\kappa(N+1)$. However, the temperature, pressure, and chemical potential of each component throughout all phases should be uniform at equilibrium conditions, as will be described later. This imposes $(N+2)(\kappa-1)$ constraints. Hence, the number of independent variables, or so-called the degrees of freedom, F , necessary to define a multiphase system is given by,:

$$F = \kappa(N + 1) - (N + 2)(\kappa - 1) = N - \kappa + 2 \quad (2.2)$$

For a single-component (pure) system, the degrees of freedom is equal to three minus the number of phases. The state of the equilibrium of a vapor-liquid mixture of a pure fluid, therefore, can be determined by identifying either its pressure or its temperature.

2.2.1 Phase behavior of Pure Compounds

The phase behavior of a pure compound is shown by the pressure–temperature diagram in Fig. 2.2. All the conditions at which the vapor and liquid phases can coexist at equilibrium are shown by the line AC. Any fluid at any other pressure–temperature conditions, is unsaturated single phase as required by the phase rule. The fluid above and to the left of the line is referred to as a compressed or under saturated liquid, whereas that below and to the right of the line is called a superheated vapor or gas.

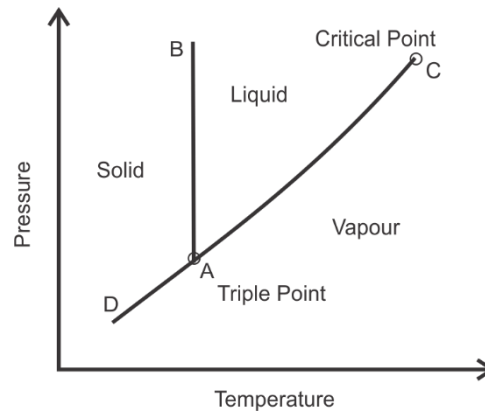
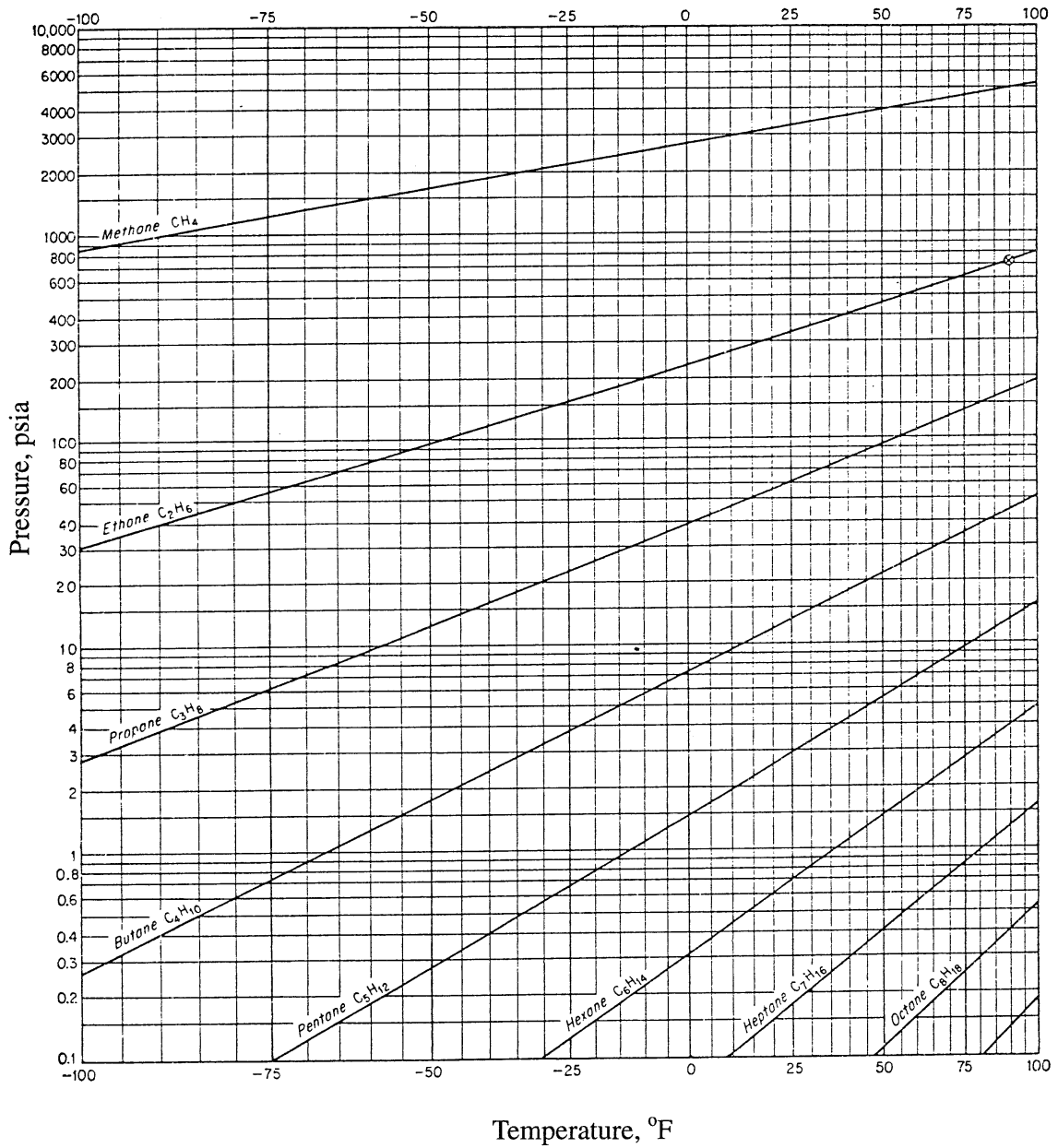


Fig. 2.2. Pressure–temperature diagram of pure substance

The line AC is commonly known as the vapor pressure curve, as it shows the pressure exerted by the vapor coexisting with its liquid at any temperature. The temperature corresponding to the atmospheric pressure is called the normal boiling point or simply the boiling point of the compound. The boiling point, T_b , of some compounds found in reservoir fluids are taken from tabled values. Fig. 2.3 shows the logarithm of vapor pressure plotted against an arbitrary temperature scale for some compounds. The scale, which is an adjusted reciprocal of the absolute temperature, has been selected so that the vapor pressures of water and most hydrocarbons can be exhibited by straight lines. This plot is known as the Cox chart. A pure substance cannot exist as liquid at a temperature above its critical temperature. Hence the vapor pressure values at temperatures above the critical temperatures, shown by Θ in Fig. 2.3, are not real, but simply extrapolated values.

The line AB on Fig. 2.2 is the solid–liquid equilibrium line, which is also known as the melting point curve. The intersection of the vapor–liquid and liquid–solid lines is the triple point. It is the only point where the three phases can coexist for a pure system.

The line AD is the solid–vapor equilibrium line or the sublimation curve. The solid carbon dioxide (dry ice) vaporizing into its gaseous form is a common example of this region of the phase behavior diagram.



$$K = (\text{°F} + 459.67) / 1.8$$

$$\text{MPa} = 0.006895 \text{ psia}$$

Fig. 2.3. Vapor pressure of normal paraffins.[8]

⊙ - Critical point

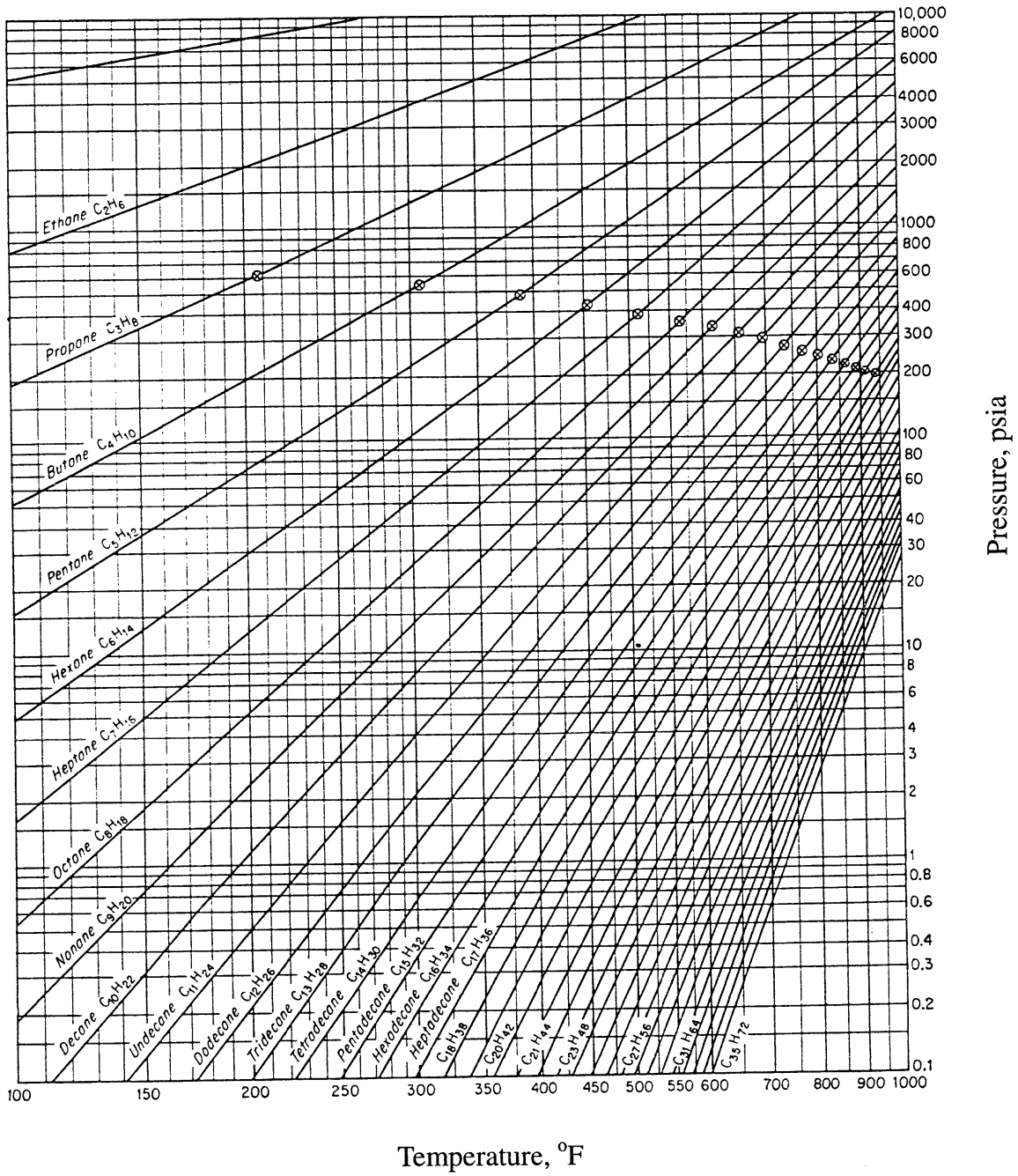


Fig. 2.3 (Cont). Vapour pressure of normal paraffins. [8].

○ - Critical point

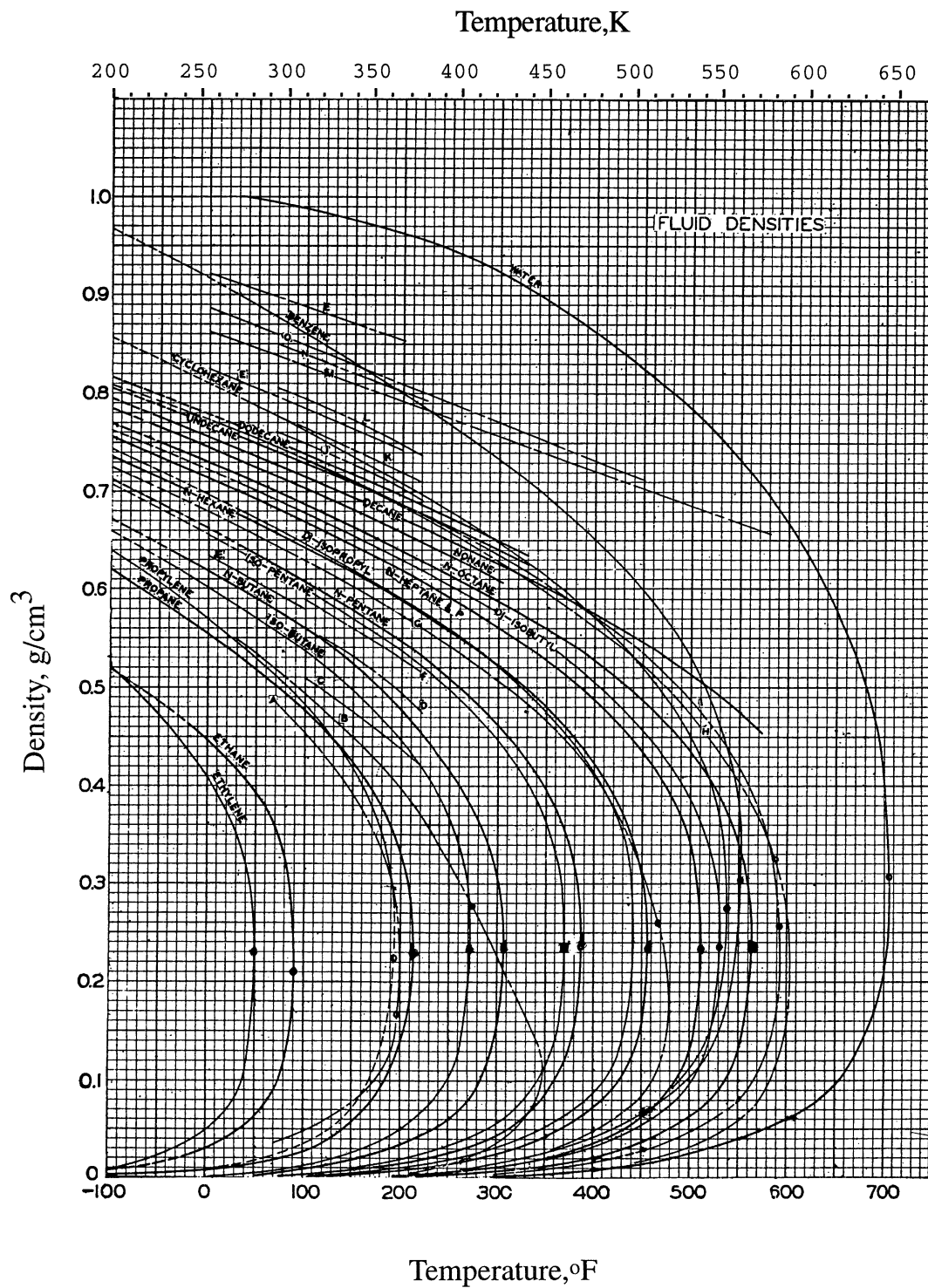


Fig. 2.4. Saturated fluid density of pure compounds (curves identified by letters are related to binary and multicomponent fluids described in [8]).

The variation of saturated fluid density with temperature for a pure compound is shown in Fig. 2.5. The densities of vapor and liquid phases approach each other as the temperature increases. They become equal at conditions known as the critical point. All the differences between the phases are reduced as the system approaches the critical point. Indeed, the phases become the same and indistinguishable at the critical point.

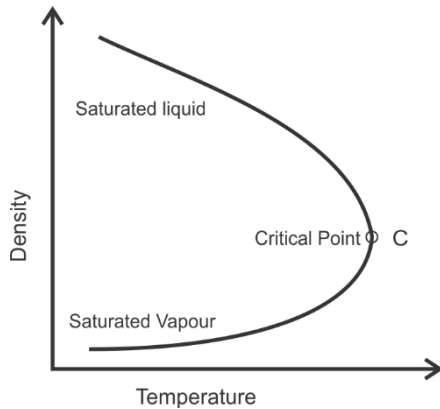


Fig. 2.5. Variations of saturated fluid density with temperature

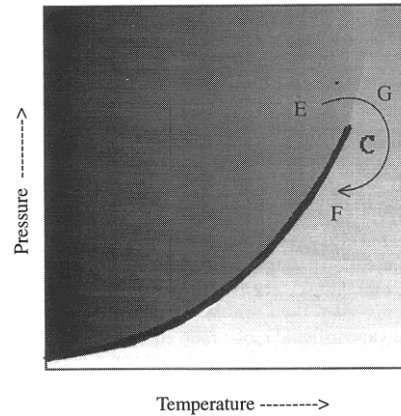


Fig. 2.6. Continuity of vapor and liquid. McGraw-Hill Companies Copyright. Reproduced from [8]

Fig. 2.4 shows the variation of saturated fluid density with temperature for a number of pure hydrocarbons. All the compounds show a similar trend, that is, the vapor and liquid densities become equal at the critical point. Other properties also show the same trend. The critical temperature, T_c , and the critical pressure, P_c , are the maximum temperature and pressure at which a pure compound can form coexisting phases.

The terms vapor and liquid are referred to the less and the more dense phases of a fluid at equilibrium. Hence, a pure compound at a temperature above its critical value cannot be called either liquid or vapor. The continuity of vapor and liquid is schematically shown in Fig. 2.6. The density at each point is shown by the shading intensity, where the darker shading corresponds to a higher density. The discontinuity across the vapor–pressure curve becomes less significant as the temperature increases and vanishes above the critical point. The superheated vapor E can be changed gradually to the compressed liquid F, through an arbitrary path EGF, without any abrupt phase change.

The pressure–volume diagram of a pure substance is shown in Fig. 2.7. Consider the compressed liquid, Point A, at a temperature below the critical temperature. The reduction of fluid pressure at constant temperature increases its volume. As the liquid is relatively incompressible the fluid expansion is small until the vapor pressure is reached, at Point B, where the first bubble evolves. Further expansion of the system results in changing the liquid into the vapor phase. For a pure substance the pressure remains constant and equal to the vapor pressure, a consequence of the phase rule, until the last drop of the liquid vaporizes. Point D. This point, where the vapor is in equilibrium with an infinitesimal amount of liquid is called the dew point.

The system bubble points at various temperatures form the bubble point curve, whereas the dew points form the dew point curve. The two curves meet at the critical point and together identify the phase envelope. Any fluid within the phase envelope, Point M, forms two equilibrated phases with the vapor/liquid molar ratio equal to BM/MD . The bubble point and dew point curves appear as a single vapor pressure curve on a pressure–temperature plot for a pure compound, Fig. 2.2.

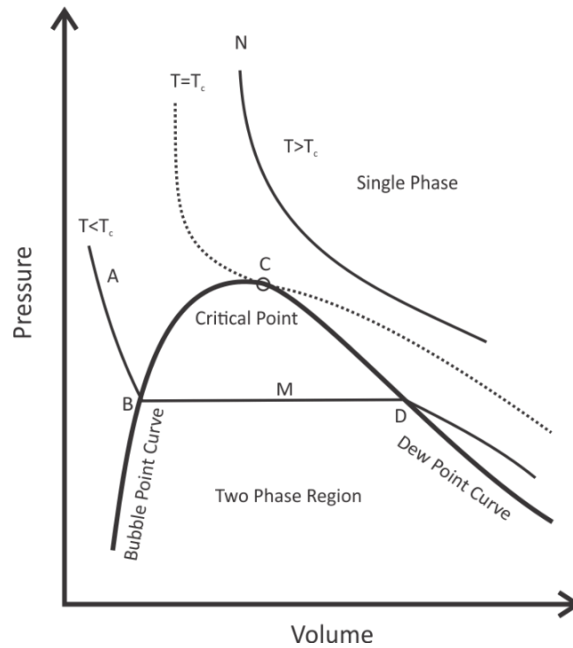


Fig. 2.7. Pressure–volume diagram of pure fluids.

The change of phase from liquid to vapor is accompanied by a large increase in volume at low temperatures (Fig. 2.7). The expansion reduces as the temperature approaches the critical point. Indeed the system changes from all liquid into all vapor, or vice versa, without any change in the mixture volume at the critical point. An isothermal expansion of a fluid at a temperature above the critical temperature does not result in any phase change. Point N. This fluid is called a supercritical fluid.

2.2.2 Corresponding States

All gases behave ideally when the pressure approaches zero. The pressure volume relation for an ideal gas is.

$$Pv = RT \quad (2.3)$$

where

- v is the molar volume,
- P is (absolute) pressure,
- T is (absolute) temperature
- R is the universal gas constant

Hence one mole of any ideal gas occupies the same volume at a given pressure and temperature. In engineering applications, gases at the standard conditions can be treated as ideal. The occupied volume of one mole of gas at various standard conditions, calculated by Eq.(2.3), is given in Tbl. 2.1.

Tbl. 2.1. Molar volume of ideal gas at various standard conditions.

Unit	Temperature	Pressure	Volume
Field	60.0 degF	14.69 psia	380 ft ³ /lbmol
Metric	273.15 K	1 atm	22.414 m ³ /kgmol
SI	288 K	100 kPa	23.95 m ³ /kgmol

As one mole of a hydrocarbon gas and one mole of air occupy the same volume at the standard conditions, the specific gravity of gas relative to air (relative density), γ_g , is simply determined by,

$$\gamma_g = \frac{M_g}{M_{air}} \quad (2.4)$$

where,

M_g is the molecular weight (molar mass) of the gas mixture

M_{air} is the molecular weight (molar mass) of air, equal to 28.96 kg/kgmol.

The universal gas constant R values are listed in Tbl. 2.2:

Tbl. 2.2. Universal gas constant values

Pressure P	Temperature T	v mole Vol	R
atm	K	cm ³ /gmol	82.0567
bar	K	liter/gmol	0.083144
MPa	K	m ³ /kgmol	0.0083144
psia	°R	ft ³ /lbmol	10.732

Due to intermolecular forces real gases do not behave ideally, particularly at elevated pressures. Eq.(2.3) is extended to real systems by including a compressibility factor, Z, as,

$$Pv = ZRT \quad (2.5)$$

The compressibility factor can be determined from various theoretical–empirical equations of state, or determined from a generalized chart for gases as shown in Fig. 2.8. Note that the compressibility factor depends only on the ratio of temperature to critical temperature (absolute), the reduced temperature, T_r , and the ratio of pressure to critical pressure, the reduced pressure, P_r .

The above approach is based on a very important concept, known as the corresponding states principle, which states that substances behave similarly when they are at the same relative proximity to their critical points. This implies that all substances behave similarly at their critical points, hence, should have equal critical compressibility factor, Z_c .

$$Z_c = \frac{P_c v_c}{RT_c} \quad (2.6)$$

The real value of critical compressibility factor, however, is not the same for all compounds (Tbl. 2.3). The compressibility chart, however, provides reliable estimates particularly for supercritical gases and at low pressure conditions. Charts relating the compressibility factor to the reduced pressure and temperature, similar to Fig. 2.8, but specific to compounds such as methane, ethane, propane, have been produced to improve the accuracy of predicted values [10].

Application of the corresponding states principle to the vapor pressure of pure compounds, follows a similar trend. The logarithm of vapor pressure of pure compounds approximately varies linearly with the reciprocal of temperature as shown in Fig. 2.3. It can be expressed, therefore, as

$$\log\left(\frac{P^s}{P_c}\right) = \zeta_1 - \frac{\zeta_2}{\left(\frac{T}{T_c}\right)} \quad (2.7)$$

where P^s is the vapor pressure and ζ_1 and ζ_2 are constants for each substance.

At the critical point $P^s/P_c = T/T_c = 1$, hence ζ_1 and ζ_2 and,

$$\log(P_r^s) = \zeta_1 \left(1 - \frac{1}{T_r}\right) \quad (2.8)$$

If the corresponding states principle were exact, the vapor pressure curves of all the compounds, plotted in the reduced form, should have the same slope, that is equal ζ_1 , falling on the same line. In practice, this does not occur.

The deviation of models based on the two parameter corresponding states principle is due to differences in molecular structures of various compounds, resulting in different intermolecular forces. The inclusion of a third parameter, additional to the reduced temperature and pressure, which concurs to the molecular structure should improve the reliability of the corresponding states principle.

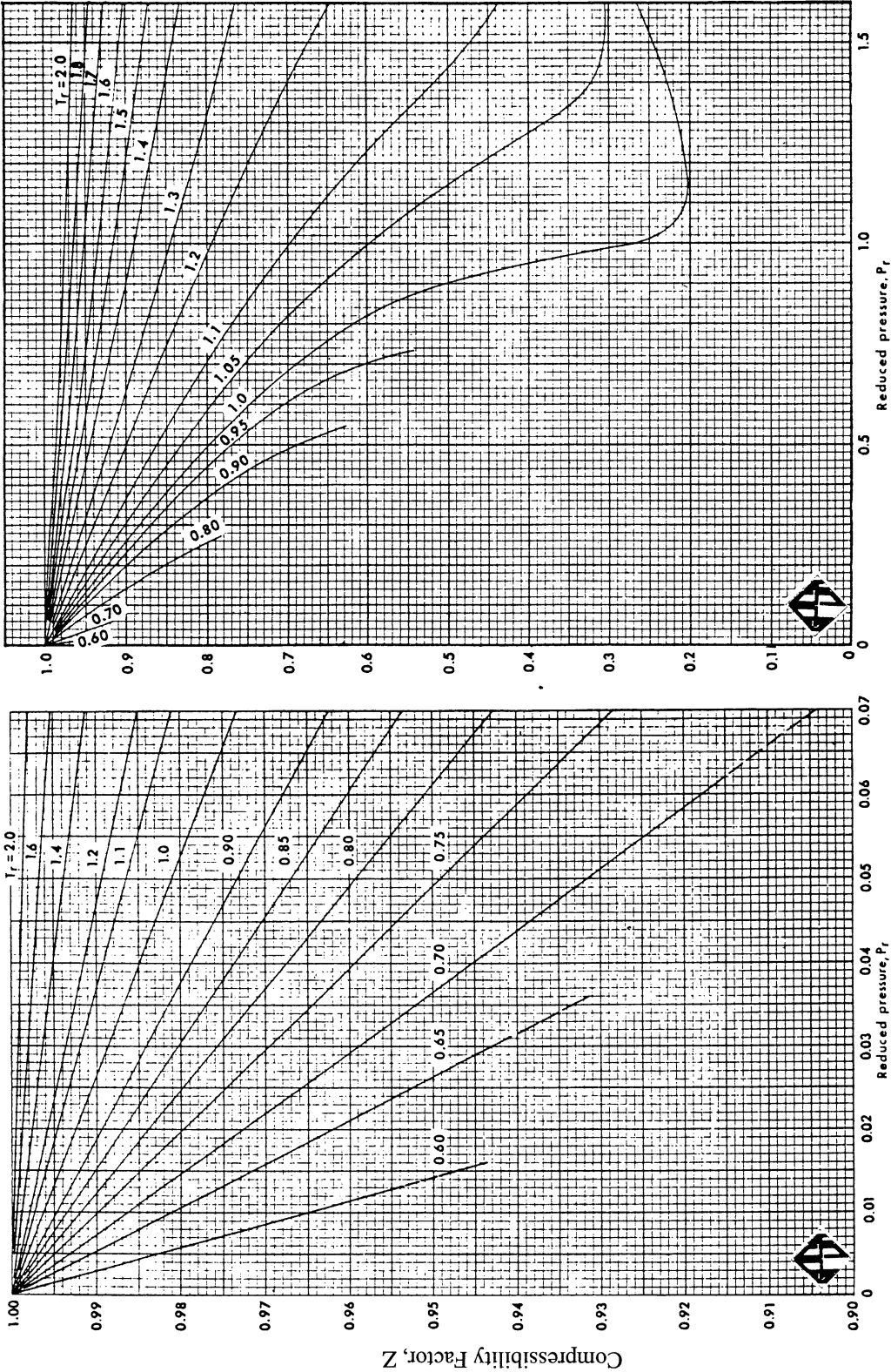


Fig. 2.8. Compressibility chart for low pressure gases. [9]

Pitzer [11] noticed that the reduced vapor pressure curves of simple spherical molecules, such as argon, krypton and xenon, indeed lie on the same curve with a reduced vapor pressure of 0.1 at the reduced temperature of 0.7. Hence, for other substances he selected the deviation of the reduced vapor pressure curve from that of spherical molecules at $T_r = 0.7$ as the third parameter of the corresponding states principle, and introduced the acentric factor, as,

$$\omega = -\log\left(\frac{P^s}{P_c}\right)_{(at\ T_r=0.7)} - 1 \quad (2.9)$$

The above definition gives an acentric factor of zero for simple spherical molecules, and positive values for other compounds except hydrogen and helium. The acentric factor generally increases with increasing size of homologue hydrocarbons. The values of acentric factor for some compounds are given in Tbl. 2.3.

The acentric factor has been widely accepted as the third parameter in generating generalized correlations, based on the corresponding states principle, particularly those related to fluid phase equilibria. For example, the vapor pressure of pure compounds can be reliably estimated using the Lee and Kesler [12] correlation, which is based on the three parameter corresponding states,

$$\frac{P^s}{P_c} = \exp(f^{(0)} - \omega f^{(1)}) \quad (2.10)$$

where, $f^{(0)}$ and $f^{(1)}$ are functions of the reduced temperature,

$$f^{(0)} = 5.92714 - \frac{6.09648}{(T_r)} - 1.28862 \ln(T_r) + 0.16934(T_r)^6$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{(T_r)} - 13.4721 \ln(T_r) + 0.43577(T_r)^6$$

Example 2.1.

Calculate the vapor pressure of normal hexane at 355.15 K, using:

- (a) the Cox chart
- (b) the Lee–Kesler equation.

Solution:

- (a) From Fig. 2.3, at $T=355.15\text{ K}$ ($179.6\text{ }^\circ\text{F}$), the vapour pressure is read equal to 0.15 MPa (21 psia).
- (b) The critical properties of normal hexane are from Tbl. 2.3, and used in Eq. (2.10) to calculate the vapor pressure as follows:

T_c, K	P_c, MPa	ω	T_r	$f^{(0)}$	$f^{(1)}$	P^s, MPa
507.6	3.025	0.3013	0.69966	-2.306192	-2.306921	0.1504

The use of critical compressibility factor as the third parameter for developing generalized correlations to predict volumetric data has also proved successful. An example is the Rackett equation [13] for the saturated molar volume of pure compounds,

$$v^s/v_c = Z_c^{(1-T_r)^{2/7}} \quad (2.11)$$

Where:

- v^s is saturated liquid volume
- v_c is critical molar volume

A more reliable estimation of the liquid molar volume is expected from the modification of the Rackett equation by Spencer and Banner [14], where the critical compressibility factor has been replaced by the parameter Z_{RA} , known as the Rackett compressibility factor,

$$v^s = \left(\frac{RT_c}{P_c} \right) Z_{RA}^{[1+(1-T_r)^{2/7}]} \quad (2.12)$$

The values of Z_{RA} for some substances [15] are given in Tbl. 2.3. For other compounds, it can be estimated from the Yamada–Gunn correlation [16]:

$$Z_{RA} = 0.29056 - 0.08775 \omega \quad (2.13)$$

The application of acentric factor and critical compressibility factor in developing generalized correlations will be described further, particularly in the chapter dealing with equations of states.

Example 2.2.

Calculate the density of saturated normal butane liquid at 393 K, using the Rackett equation.

A cylinder contains 1 kg of saturated liquid butane at 393 K. What is the volume of liquid butane remaining in the cylinder after consuming 0.5 kg of butane?

Solution:

Reading the critical properties of normal butane from Tbl. 2.3 and substituting them in Eq.(2.12), at 393 K, we obtain:

M kg/kgmol	T_c K	P_c MPa	Z_{RA}	T_r	v^s m ³ /mol	Density kg/m ³
58.123	425.12	3.796	0.2730	0.92444	0.13665	425.3

where the density, ρ^s has been calculated as,

$$\rho^s = M/v^s$$

The volume of cylinder, containing 1kg of the saturated liquid butane, is:

$$V = m/\rho = 1/425.3 = 0.002351 \text{ m}^3$$

The cylinder pressure remains constant, equal to the normal butane vapor pressure, as long as the mixture remains two phases at 393 K. The vapor pressure can be calculated from the Lee–Kesler equation, Eq.(2.10), similar to that in Example 2.1, which results in:

$$P^s = 2.2160 \text{ MPa, at 393 K.}$$

The vapor density at the above conditions can be calculated from Eq. (2.7).

The compressibility factor, Z, is read from Fig. 2.8, at prevailing reduced values of:

$$P_r = P/P_c = 2.216/3.796 = 0.5838 \text{ and } T_r = 0.9244, \text{ to be } Z = 0.67.$$

The universal gas constant given from Tables, to be 0.0083144 MPa.m³/(K kg mol).

Hence,

$$v = ZRT/P = 1.003 \text{ m}^3/\text{kg mol, and the vapor density is ,}$$

$$\rho^v = M/v^v = 58.123/1.003 = 57.95 \text{ kg/m}^3$$

The mass balance results in,

$$m = V^l \rho^s + V^v \rho^v$$

$$0.5 = V^l \cdot 425.3 + (0.002351 - V^l) \cdot 57.95$$

$$\text{Liquid butane volume, } V^l = 0.0009902 \text{ m}^3$$

Tbl. 2.3. Properties of pure compounds.

	M kg/kgmol	T _b K	T _c K	P _c MPa	v _c m ³ /kgmol	Z _c	acentric factor ω	Rackett Z _{RA}	Parachor **	Sp.gr
Methane	16.043	111.66	190.56	4.599	0.0986	0.2862	0.0115	0.28941	74.05	0.3000
Ethane	30.070	184.55	305.32	4.872	0.1455	0.2793	0.0995	0.28128	112.91	0.3562
Propane	44.096	231.11	369.83	4.248	0.2000	0.2763	0.1523	0.27664	154.03	0.5070
i-Butane	58.123	261.43	408.14	3.648	0.2627	0.2824	0.1770	0.27569	185.32	0.5629
n-Butane	58.123	272.65	425.12	3.796	0.2550	0.2739	0.2002	0.27331	193.90	0.5840
1-Pentane	72.150	300.99	460.43	3.381	0.3058	0.2701	0.2275	0.2706*	229.37	0.6247
Neopentane	72.150	282.65	433.78	3.199	0.3036	0.2693	0.1964	0.27570	236.00	0.5974
n-Pentane	72.150	309.22	469.7	3.370	0.3130	0.2701	0.2515	0.26853	236.00	0.6311
2-Methylpentane	86.177	333.41	497.5	3.010	0.3664	0.2666	0.2781	0.2662*	269.15	0.6578
n-Hexane	86.177	341.88	507.6	3.025	0.371	0.2659	0.3013	0.26355	276.71	0.6638
n-Heptane	100.204	371.58	540.2	2.740	0.428	0.2611	0.3495	0.26074	318.44	0.6882
n-Octane	114.231	398.83	568.7	2.490	0.486	0.2559	0.3996	0.25678	359.33	0.7070
n-Nonane	128.258	423.97	594.6	2.290	0.544	0.2520	0.4435	0.25456	399.57	0.7219
n-Decane	142.285	447.3	617.7	2.110	0.600	0.2465	0.4923	0.25074	440.69	0.7342
n-Undecane	156.312	469.08	639	1.949	0.659	0.2419	0.5303	0.24990	482.00	0.7445
n-Dodecane	170.338	489.47	658	1.820	0.716	0.2382	0.5764	0.24692	522.26	0.7527
n-Tridecane	184.365	508.62	675	1.680	0.775	0.2320	0.6174	0.24698	563.77	0.7617
n-Tetradecane	198.392	526.73	693	1.570	0.830	0.2262	0.6430	0.24322	606.05	0.7633
n-Pentadecane	212.419	543.83	708	1.480	0.889	0.2235	0.6863	0.2303*	647.43	0.7722
n-Hexadecane	226.446	560.01	723	1.400	0.944	0.2199	0.7174	0.2276*	688.50	0.7772
n-Heptadecane	240.473	575.3	736	1.340	1.000	0.2190	0.7697	0.23431	730.05	0.7797
n-Octadecane	254.500	589.86	747	1.270	1.060	0.2168	0.8114	0.22917	771.95	0.7820
n-Nonadecane	268.527	603.05	758	1.210	1.120	0.2150	0.8522	0.2158*	813.85	0.7869
n-Eicosane	282.553	616.93	768	1.160	1.170	0.2126	0.9069	0.22811	853.67	0.7924
n-Heneicosane	296.580	629.7	781.7	1.147	1.198	0.2114	0.9220	0.2097*	897.64	0.7954
n-Docosane	310.610	641.8	791.8	1.101	1.253	0.2095	0.9550	0.2068*	939.55	0.7981
n-Tricosane	324.630	653.4	801.3	1.059	1.307	0.2078	0.9890	0.2038*	981.43	0.8004
n-Tetracosane	338.680	664.4	810.4	1.019	1.362	0.2061	1.0190	0.2011*	1023.40	0.8025
Ethylene	28.054	169.47	282.36	5.032	0.1291	0.2767	0.0852	0.28054	101.53	0.5000
Propylene	42.081	225.43	364.76	4.612	0.1810	0.2753	0.1424	0.27821	143.02	0.5210
1-Butene	56.107	266.9	419.59	4.020	0.2399	0.2765	0.1867	0.27351		0.6005
cis-2-Butene	56.107	276.87	435.58	4.206	0.2340	0.2717	0.2030	0.27044		0.6286
trans-2-Butene	56.107	274.03	428.63	4.103	0.2382	0.2742	0.2182	0.27212		0.6112
Propadiene	40.065	238.65	393.15	5.470	0.1620	0.2711	0.1596	0.27283		0.5997
1 2-Butadiene	54.092	284	444	4.500	0.2190	0.2670	0.2509	0.2685*		0.6576
1 3-Butadiene	54.092	268.74	425.37	4.330	0.2208	0.2704	0.1932	0.27130		0.6273
1-Pentene	70.134	303.11	464.78	3.529	0.2960	0.2703	0.2329	0.27035		0.6458
cis-2-Pentene	70.134	310.08	475.93	3.654	0.3021	0.2790	0.2406	0.2694*		0.6598
trans-2-Pentene	70.134	309.49	475.37	3.654	0.3021	0.2793	0.2373	0.2697*		0.6524
2-Methyl-1-Butene	70.134	304.3	465	3.400	0.2920	0.2568	0.2287	0.2705*		0.6563
3-Methyl-1-Butene	70.134	293.21	450.37	3.516	0.3021	0.2837	0.2286	0.2705*		0.6322
2-Methyl-2-Butene	70.134	311.71	471	3.400	0.2920	0.2535	0.2767	0.2663*		0.6683
1-Hexene	84.161	336.63	504.03	3.140	0.3540	0.2653	0.2800	0.2660*		0.6769
1-Heptene	98.188	366.79	537.29	2.830	0.4130	0.2616	0.3310	0.2615*		0.7015
Cyclopentane	70.134	322.4	511.76	4.502	0.2583	0.2733	0.1943	0.26824	210.05	0.7603
Methylcyclopentane	84.161	344.96	532.79	3.784	0.3189	0.2725	0.2302	0.2704*		0.7540
Cyclohexane	84.161	353.87	553.54	4.075	0.3079	0.2726	0.2118	0.27286	247.89	0.7835
Methylcyclohexane	98.188	374.08	572.19	3.471	0.3680	0.2685	0.2350	0.26986	289.00	0.7748
Ethylcyclopentane	98.188	376.62	569.52	3.397	0.3745	0.2687	0.2715	0.2667*		0.7712
Ethylcyclohexane	112.215	404.95	609.15	3.040	0.4500	0.2701	0.2455	0.2690*	328.74	0.7921
Benzene	78.114	353.24	562.16	4.898	0.2589	0.2714	0.2108	0.26967	210.96	0.8829
Toluene	92.141	383.78	591.79	4.109	0.3158	0.2637	0.2641	0.2639*	252.33	0.8743
Ethylbenzene	106.167	409.35	617.17	3.609	0.3738	0.2629	0.3036	0.26186	292.27	0.8744
o-Xylene	106.167	417.58	630.37	3.734	0.3692	0.2630	0.3127	0.2620*		0.8849
m-Xylene	106.167	412.27	617.05	3.541	0.3758	0.2594	0.3260	0.2620*		0.8694
p-Xylene	106.167	411.51	616.26	3.511	0.3791	0.2598	0.3259	0.2870*		0.8666
Nitrogen	28.014	77.35	126.1	3.394	0.0901	0.2917	0.0403	0.28971	61.12	0.8094
Oxygen	31.999	90.17	154.58	5.043	0.0734	0.2880	0.0218	0.28962		1.1421
Carbon Monoxide	28.010	81.7	132.92	3.499	0.0931	0.2948	0.0663	0.28966		
Carbon Dioxide	44.010	194.67	304.19	7.382	0.0940	0.2744	0.2276	0.27275	82.00	0.8180
Hydrogen Sulphide	34.082	212.8	373.53	8.963	0.0985	0.2843	0.0827	0.28476	85.50	0.8014
Sulpher Dioxide	64.065	263.13	430.75	7.884	0.1220	0.2686	0.2451	0.26729		1.3946
Hydrogen	2.016	20.39	33.18	1.313	0.0642	0.3053	-0.2150	0.31997		
Water	18.015	373.15	647.13	22.055	0.0560	0.2294	0.3449			1.0000

* Z_{RA} from [1.15] except those identified by * which are calculated from the Yamada-Gunn correlation, Eq. 2.13).

** Parachor values are to be used only in Eq.(8.21).

2.2.3 Multicomponent Mixtures

The phase behavior of a multi-component system is more elaborate than that of a pure compound. The complexity generally compounds as components with widely different structures and molecular sizes comprise the system. Reservoir fluids are mainly composed of hydrocarbons with similar structures. Their phase behavior, therefore, is not generally highly complex.

The phase behavior of a binary system, although relatively simple, is very much similar to a real multi-component reservoir fluid. It is, therefore, an appropriate substitute for explaining the qualitative behavior of reservoir hydrocarbon mixtures.

The phase rule indicates that in a binary vapor-liquid system, both the temperature and the pressure are independent variables. The pressure-temperature diagram of a binary mixture is schematically shown in Fig. 2.9. The phase envelope, inside which the two phases coexist, is bounded by the bubble point and dew point curves. The two curves meet at the critical point (C), where all differences between the two phases vanish and the phases become indistinguishable. Note that the two phases can coexist at some conditions above the critical point. The highest pressure (B) and the highest temperature (D) on the phase envelope are called the cricondenbar and the cricondentherm, respectively.

The pressure-volume diagram of a binary mixture is schematically shown in Fig. 2.10. Note that the system pressure decreases during an isothermal expansion between its bubble and dew points, contrary to that for a pure compound.

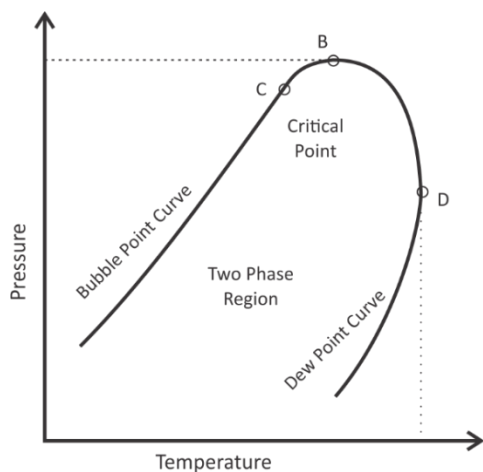


Fig. 2.9. Schematic pressure-temperature diagram of a binary mixture.

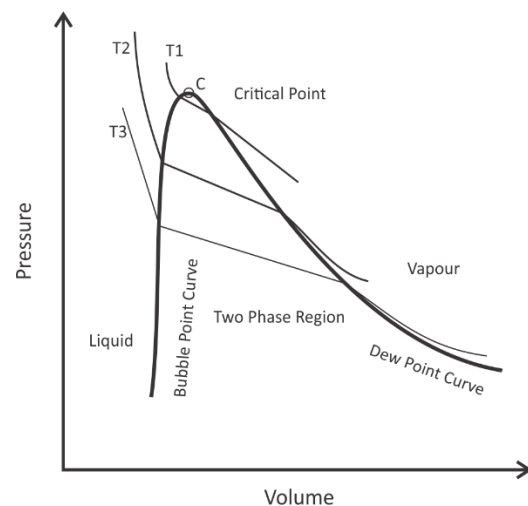


Fig. 2.10. Pressure-volume diagram of binary mixtures.

The phase diagram of a mixture is determined by its composition. Fig. 2.11 shows the phase diagram of ethane-heptane system. The critical temperature of different mixtures lies between the critical temperatures of the two pure compounds. The critical pressure, however, exceeds the values of both components as pure, in most cases. The locus of critical points is shown by the dashed line in Fig. 2.11. The greater the difference between the critical points of the two components, the higher the mixture critical pressure can rise as shown in Fig. 2.12. No binary mixture can exist as a two-phase system outside the region bounded by the locus of critical points.

The corresponding states principle, described for pure substances, is also used for multicomponent systems. Pseudo critical values are used, however, instead of true critical properties in applying fluid models developed for pure substances, such as those in Fig. 2.8, and Eq. (2.11).

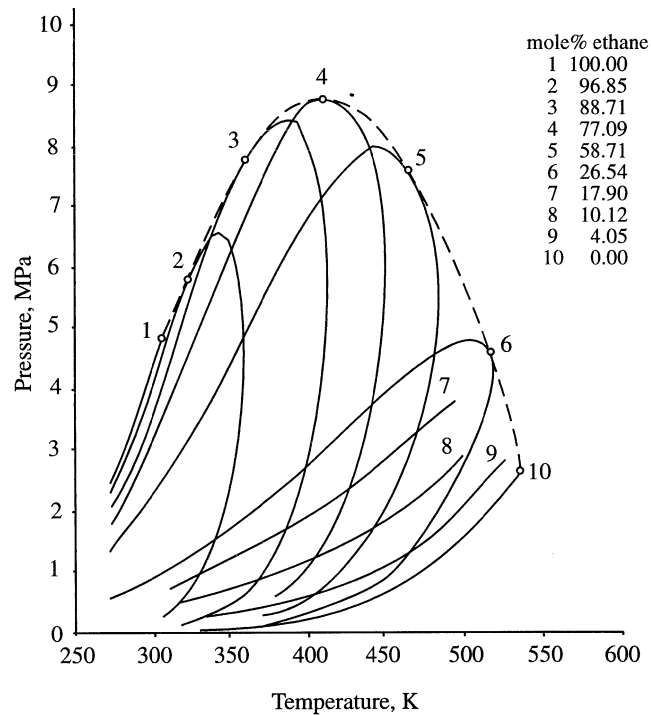


Fig. 2.11. Phase diagram of ethane – n-heptane Mixtures. [8]

Pseudo critical properties of a mixture are calculated by applying a mixing rule to the critical properties of its constituents. A number of mixing rules have been proposed, but molar averaging, also known as Kay's mixing rule, is the most common rule,

$${}_p\theta_c = \sum_i z_i \theta_{c_i} \quad (2.14)$$

where z_i is the mole fraction, ${}_p\theta_c$ is any pseudo critical property, such as temperature, pressure, and volume, and θ_{c_i} is the critical property of component i . Properties scaled relative to the pseudo critical values are referred to as pseudo reduced properties, such as pseudo reduced temperature:

$${}_pT_r = \frac{T}{{}_pT_c} \quad (2.15)$$

and pseudo reduced pressure

$${}_pP_r = \frac{P}{{}_pP_c} \quad (2.16)$$

The true critical properties, however, are different from the pseudo values calculated by averaging. The true critical pressure often shows the highest deviation from the pseudo value, as evidenced in Fig. 2.12. The prediction of true critical properties will be described later.

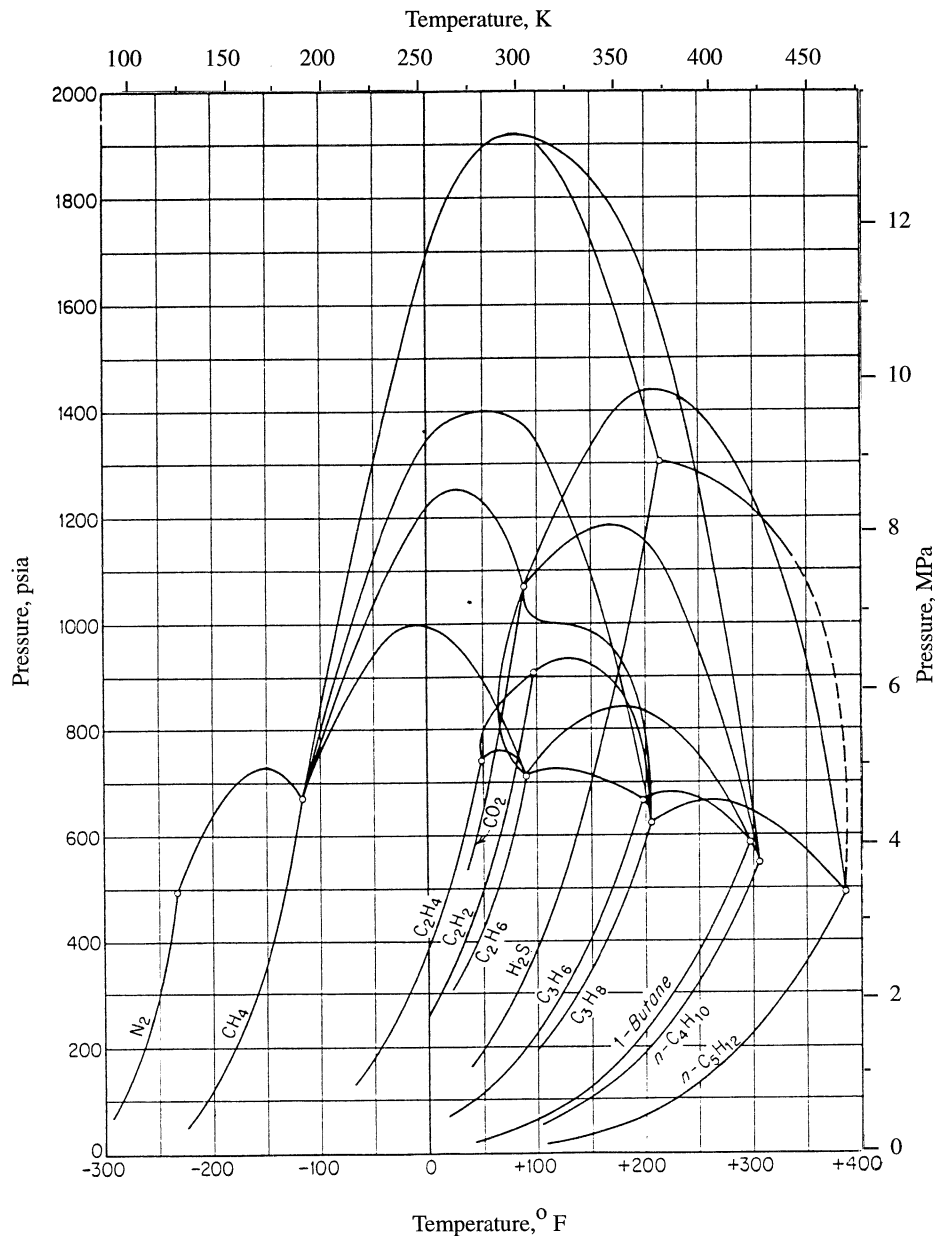


Fig. 2.12. Critical loci for binary mixtures. Redrawn after [8].

A typical phase diagram of multi-component system at constant composition is shown in Fig. 2.13. Vapor and liquid phases coexist at any pressure–temperature conditions within the phase envelope. The liquid/mixture volumetric ratios are shown by the constant quality lines. Note that the distance between iso–volume or quality lines decreases as the critical point is approached. Small pressure or temperature changes at a region near the critical point cause major phase changes.

An isothermal reduction of pressure for a vapor–like fluid. Point A, forms the first drop of liquid at the dew point, Point B. Further reduction of pressure will result in further condensation, as indicated by the quality lines. This phenomenon is known as the retrograde condensation. The condensation will cease at some point. Point D, and the condensed phase will revaporize by further reduction of pressure. The shaded region of the phase diagram, where pressure reduction results in condensation is referred to as die retrograde region. Note that the above behavior occurs only if the gas temperature lies between the critical temperature and the cricondentherm. Fig. 2.13 shows that there are two dew point pressures at any temperature for retrograde gases. The upper dew point is sometimes called the

retrograde dew point. The lower dew point is of little practical significance for most gas condensate fluids.

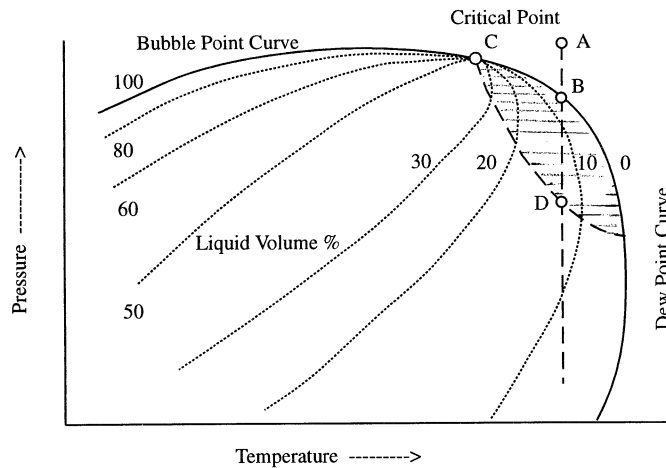


Fig. 2.13. Phase diagram of a multicomponent mixture.

The relative position of the critical point to the cricondenbar and the cricondenbar on the phase envelope can lead to other retrograde phenomena. Fig. 2.14 shows that an isobaric increase of temperature from point 1 to point 2 results in condensation. This behavior, which can also be called retrograde condensation, is of little interest in reservoir operations. It indicates, however, that raising the temperature of a high-pressure rich gas may not be a proper procedure to avoid condensation in fluid handling. The vaporization of liquid by isobaric temperature decrease, shown in Fig. 2.15, or by isothermal pressure increase is known as retrograde vaporization.

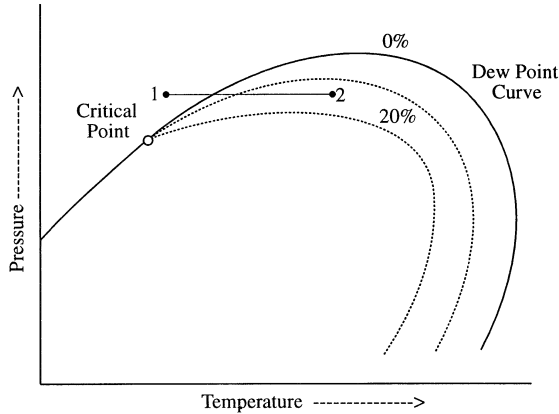


Fig. 2.14. Retrograde condensation at constant pressure.

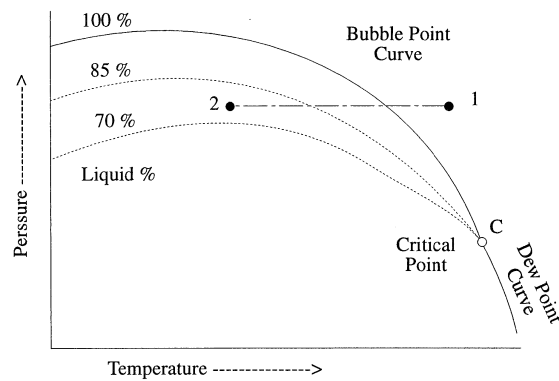


Fig. 2.15. Retrograde vaporisation at constant pressure.

The vapor-liquid phase diagram of a typical multi-component system, Fig. 2.13, describes the behavior of reservoir fluids in most cases. There are, however, exceptional cases. Weinaug and Bradley [17] observed an unusual behavior for a naturally occurring hydrocarbon mixture as shown in Fig. 2.16. Note that an isothermal reduction of pressure, e.g. at 160°F, results in an increase of the liquid volume after an initial normal behavior. A similar behavior has also been reported [18] for a multicomponent hydrocarbon oil, as shown in Fig. 2.17. Note that the gas/liquid volumetric ratio increases initially below the bubble point, as expected. The trend reverses over a limited pressure range, prior to behaving normally again. The calculated gas to liquid ratio in molar term is shown also in Fig. 2.17. The ratio increases very gradually over the whole tested pressure range, without any peculiarity. The

reason for the apparent disagreement between the two plots, is the change in molar volumes of the two phases.

A single phase hydrocarbon reservoir fluid may form more than two phases during depletion. Solid, or semi-solid phases, such as asphaltenes can form at some conditions. A high pressure gas, rich in hydrocarbon compounds of different homologous series, may condense two immiscible liquid phases, each rich with one structural type of molecules. Gas mixtures rich in CO₂ or H₂S at low temperatures can form a rich liquid phase immiscible with the hydrocarbon rich condensate phase.

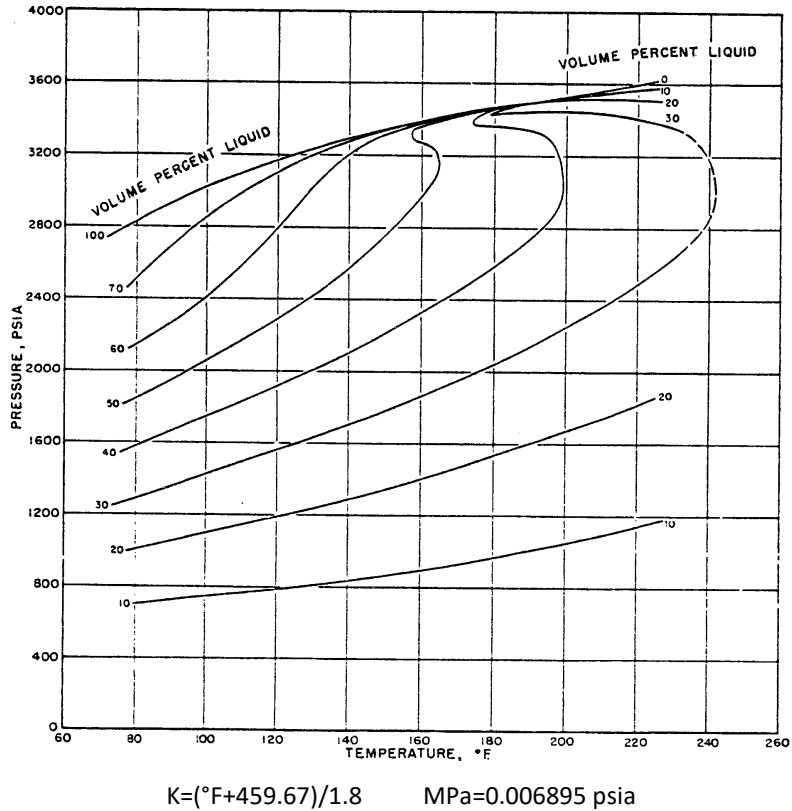


Fig. 2.16. Phase diagram of a hydrocarbon mixture. After [17].

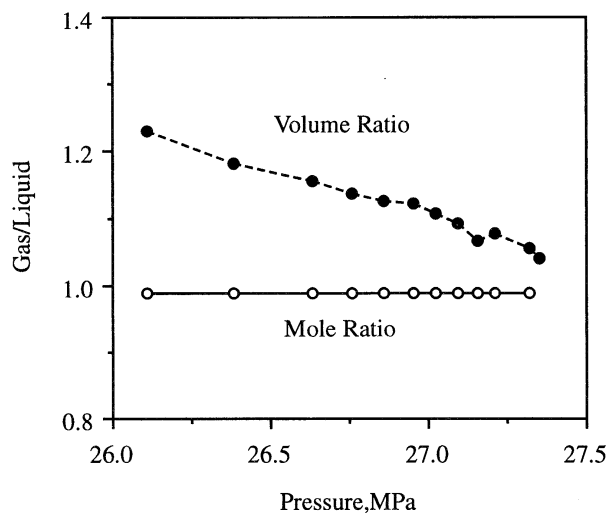


Fig. 2.17. Variations of gas to liquid ratio by reducing pressure below bubble point. After [18].

2.3 CLASSIFICATION OF RESERVOIR FLUIDS

The typical phase diagram of a reservoir hydrocarbon system, shown in Fig. 2.13, can be used conveniently to describe various types of reservoir fluids. A reservoir contains gas if its temperature is higher than the fluid critical temperature, otherwise it contains oil. The depletion of reservoir will result in retrograde condensation in the reservoir if the reservoir temperature lies between the critical temperature and the cricondentherm, whereas no liquid will form if it is above the cricondentherm. The oil in a reservoir with a temperature close to its critical point is more volatile than that at a lower temperature. A small reduction of pressure below the bubble point, in a reservoir with a temperature just below the fluid critical temperature, may vaporize half the oil volume. It is evident, therefore, that the location of reservoir temperature on the phase diagram can be used to classify reservoir fluids.

The temperature of a reservoir is determined by its depth. The phase behavior of a reservoir fluid is determined by its composition. Typical compositions of various classes of reservoir hydrocarbon fluids are given in Tbl. 2.4.

Tbl. 2.4. Typical compositions of various reservoir fluids

Comp.	Dry Gas Mole%	Wet Gas Mole%	Gas cond. Mole%	Near-critical Oil, Mole%	Volatile Oil, Mole%	Black Oil, Mole%
CO ₂	0.1	1.41	2.37	1.3	0.93	0.02
N ₂	2.07	0.25	0.31	0.56	0.21	0.34
C ₁	86.12	92.46	73.19	69.44	58.77	34.62
C ₂	5.91	3.18	7.8	7.88	7.57	4.11
C ₃	3.58	1.01	3.55	4.26	4.09	1.01
i-C ₄	1.72	0.28	0.71	0.89	0.91	0.76
n-C ₄		0.24	1.45	2.14	2.09	0.49
i-C ₅	0.5	0.13	0.64	0.9	0.77	0.43
n-C ₅		0.08	0.68	1.13	1.15	0.21
C _{6(s)}		0.14	1.09	1.46	1.75	1.61
C ₇₊		0.82	8.21	10.04	21.76	56.4
Σ	100	100	100	100	100	100

Critical temperatures of heavy hydrocarbons are higher than those of light compounds. Therefore, the critical temperature of hydrocarbon mixtures predominantly composed of heavy compounds is higher than the normal range of reservoir temperatures, and these fluids behave liquid-like, i.e., oil. Whereas the temperature of a reservoir mainly composed of methane, with a critical temperature of 190.6 K, will be higher than the mixture critical temperature.

When the reservoir pressure falls below the saturation point, the phase diagram of the original reservoir fluid is no longer valid. Gas and liquid phases are produced at a ratio different to that in the original combined state, resulting in changes of the overall composition. The gravitational segregation of the two phases with different densities will also inhibit the contact between the phases, hence preventing the achievement of equilibrium throughout the reservoir.

In a hydrocarbon reservoir consisting of a gas cap and an oil column two separate phase diagrams, one for each phase can be considered. The two phases are both saturated, with the saturation pressures ideally equal to the reservoir pressure at the gas-oil contact as shown in Fig. 2.18. Hence, when a saturated gas reservoir is discovered, an oil column below it is generally expected. Similarly, a saturated oil reservoir may strongly indicate the presence of a gas cap.

Petroleum reservoir fluids can be classified according to various criteria. Although identifying a fluid as gas or oil is adequate in most phase behavior studies, it is more common to classify the fluid in accordance to its volumetric behavior at the reservoir and surface conditions. This approach yields a few set of formulations, known as material balance equations, which can be appropriately applied to each class of fluid for reservoir studies.

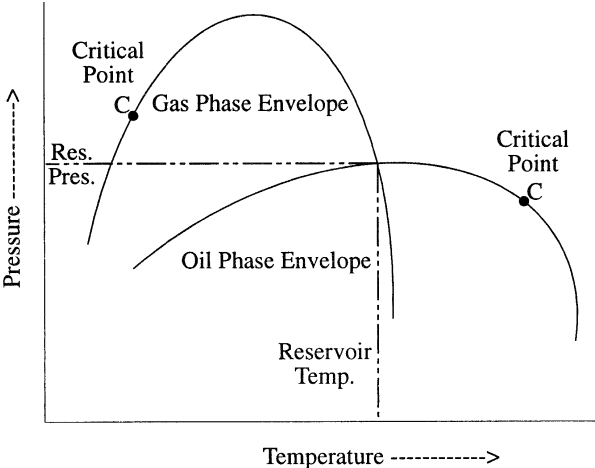


Fig. 2.18. Phase diagrams of segregated oil and gas phases in the vicinity of gas/oil contact.

The reservoir fluid is produced and measured at the surface as the stock tank oil (STO) and gas at standard conditions (V_g)_{SC}, as shown schematically in Fig. 2.19. As the material balance equations relate the produced fluids to those in the reservoir, the initial producing gas to liquid volumetric ratio is considered as the most important indicator of the class of a reservoir fluid. The gas to oil ratio, GOR, is most commonly defined as the number of cubic feet of the associated gas produced at standard conditions per barrel of stock tank oil in the Field units. For gas condensate fluids, where the produced fluid is predominantly gas, the inverse of the above definition, known as the condensate to gas ratio, CGR, is often used.

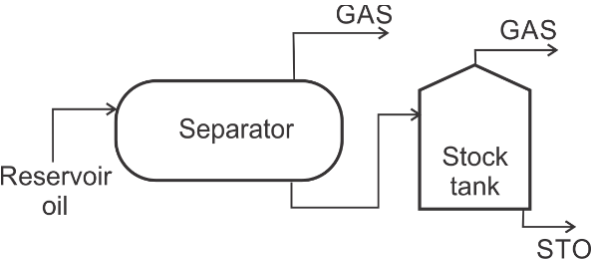


Fig. 2.19. Schematic diagram of stabilizing produced oil as stock tank oil (STO) and gas at standard conditions.

The stock tank oil gravity generally varies significantly for different classes of fluids, hence it can also be used as an indicator. The gravity is expressed as API degrees in field units,

$$^{\circ}API = \frac{141.5}{\gamma_{STO}} - 131.5 \tag{2.17}$$

Where γ_{STO} is the stock tank oil specific gravity, or relative density, to water at 60 °F (288 K). The concentration of heavy fraction, in reservoir fluid correlates reasonably well with GOR. As the stock tank oil is mostly comprised of this fraction, it can also be used as an indicator of the reservoir fluid type. Fig. 2.20 shows that an initial producing GOR of 570 v/v (3,200 SCF/STB) and 12.5 mole% are valid boundaries for gas and oil systems [19], as shown in Fig. 2.20.

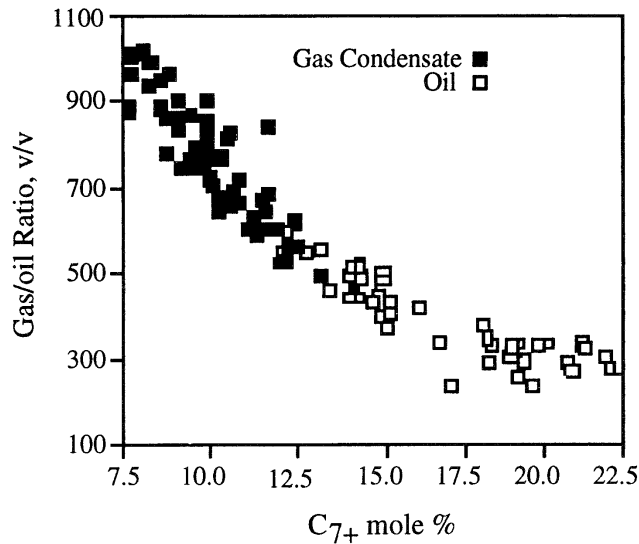


Fig. 2.20. GOR relation for typical oil and gas condensate fluids. Reproduced from [19].

The most common method of identifying petroleum reservoir fluids is to classify them as dry gas, wet gas, gas condensate (retrograde gas), volatile oil and black oil.

2.3.1 Dry Gas

Dry gases are predominantly composed of methane and non-hydrocarbons such as nitrogen and carbon dioxide. Fig. 2.21 shows the phase diagram of a dry gas. The phase envelope is relatively tight and mostly located below the ambient temperature. Note that the gas remains single phase from the reservoir to the separator conditions. Water, however, may condense at the surface conditions due to the gas cooling. PVT tests in the laboratory are limited to the gas compressibility measurement.

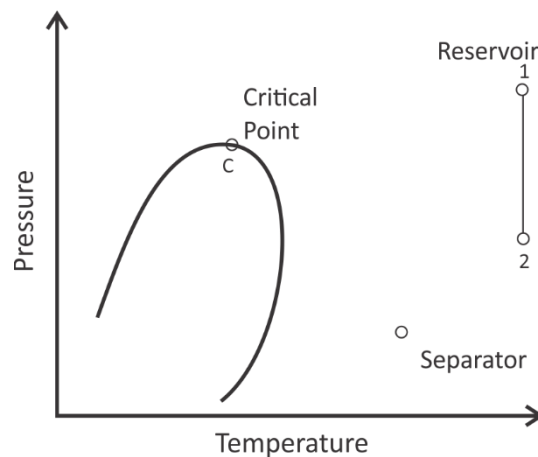


Fig. 2.21. Phase diagram of dry gas.

2.3.2 Wet Gas

A wet gas is mainly composed of methane and other light components with its phase envelope located entirely over a temperature range below that of the reservoir. A wet gas, therefore, will not drop-out condensate in the reservoir during depletion, (1) to (2), as shown in Fig. 2.22. The separator conditions lie, however, within the phase envelope, producing some condensate at the surface. Gas fields in the Southern North Sea are good examples of this type of reservoirs.

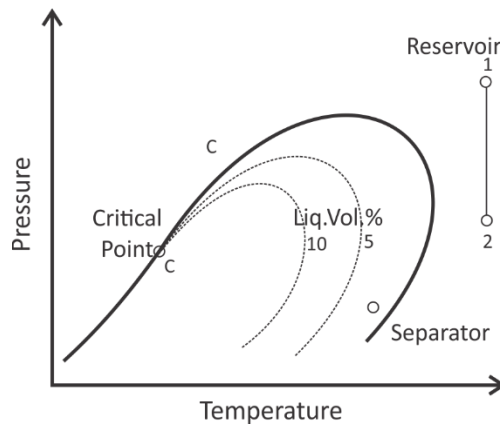


Fig. 2.22. Phase diagram of wet gas.

As no condensate is formed in the reservoir, material balance equations for a dry gas are equally suitable for a wet gas. The only PVT test required at the reservoir conditions is the gas compressibility measurement. Separator tests are generally conducted to determine the amount and properties of the condensed phase at the surface conditions.

A wet gas reservoir is commonly produced by simple blow-down, similar to a dry gas, as no condensate is formed in the reservoir. Producing gas to condensate ratios are typically above 10 000 v/v (50 000 SCF/STB) and remain constant during the entire life of the reservoir. The condensate color is usually water-white with a low specific gravity which remains unchanged during the reservoir production life.

2.3.3 Gas Condensate

A typical gas condensate phase diagram is shown in Fig. 2.23. The presence of heavy hydrocarbons expands the phase envelope relative to a wet gas, hence, the reservoir temperature lies between the critical point and the cricondentherm. The gas will drop-out liquid by retrograde condensation in the reservoir, when the pressure falls below the dew point, from (1) to (2) in Fig. 2.23. Further condensation from the produced gas also occurs at separator conditions due to cooling.

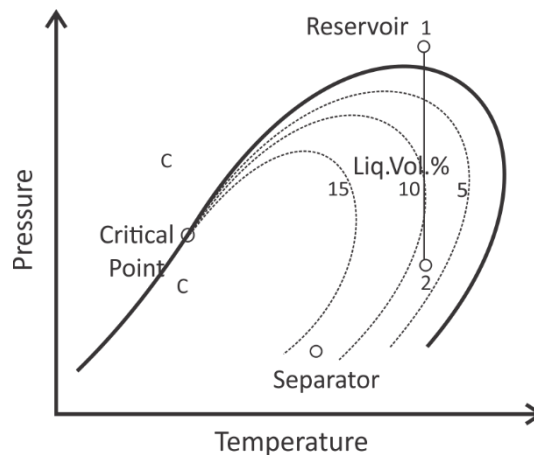


Fig. 2.23. Phase diagram of gas condensate.

The amount of potentially condensable hydrocarbons in the reservoir increases with the richness of the gas, as heavy compounds shift the critical temperature towards the reservoir temperature. Whereas a gas with a cricondentherm near the reservoir temperature will behave very much like a wet gas. Gas to liquid ratios range between 570 to 30 000 v/v (3200 to 150 000 SCF/STB)[19]. For practical purposes a gas condensate reservoir with a GOR of above 10 000 v/v (50 000 SCF/STB) can be treated

as a wet gas. The producing GOR initially remains constant until the reservoir pressure falls below the dew point and increases thereafter. For gases with GOR of above 20 000 v/v (100 000 SCF/STB), the condensation in reservoir has negligible effect on the properties of produced gas, but it can noticeably reduce the gas recovery rate.

The concentration of heptanes plus is generally less than 12.5 mole% in gas condensate fluids as fluids containing more than that almost always behave liquid like in the reservoir. Exceptional cases with condensates as high as 15.5 mole% and oils with as low as 10 mole% of heptanes plus have also been reported [20].

The condensate color can be water-white or dark. Dark condensates usually have relatively high specific gravity and are associated with high dew point gases. Condensate specific gravity ranges between 0.74 and 0.82 (60 to 40 °API), although values as high as 0.88 (as low as 29 °API) have been reported [21].

Material balance equations developed for dry gases can be used for a gas condensate reservoir as long as its pressure remains above the dew point. A compositional material balance method should be used below the dew point. It is commonly assumed that the condensate formed in reservoir remains immobile due to its low saturation, and is mostly non-recoverable. Recent results [22], however, have indicated that the condensate can flow even at very low saturations.

Fig. 2.24 shows a common characteristic of gas, condensate fluids. The liquid drop-out reaches a maximum and then decreases by vaporization during pressure depletion. This behavior may imply that when the reservoir pressure decreases sufficiently, the condensate will be recovered by revaporization. However, by the time the pressure falls below the dew point, the original phase diagram is no longer valid as the system composition changes during the production period. PVT tests simulating reservoir conditions will be described later.

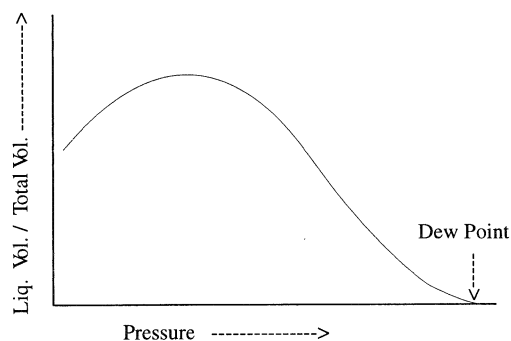


Fig. 2.24. Liquid drop-out behavior of gas condensate.

Condensation and loss of valuable compounds in reservoirs could be avoided by maintaining the reservoir pressure above the fluid dew point by gas recycling. In practice, however, this is very seldom carried out because of shortage of gas. Partial pressure maintenance is more common to minimize the losses of condensate, where it is economical to do so. In recycling operations intermediate and heavy compounds of the produced fluid are separated and the remaining lean gas is injected back into the reservoir. The recycled gas which is predominantly methane, not only reduces the pressure decline rate, but also makes the system leaner. The removal of a sufficient amount of heavy hydrocarbons from a gas condensate reservoir may ideally shift the entire phase diagram farther away from the reservoir temperature to form a wet gas reservoir. The reservoir can then be produced by blow down without much loss of valuable liquid. But the lack of complete displacement and mixing of the recycled gas with the in-situ fluid limits the success of the above operation. However, the liquid loss by depletion will be lower after recycling.

2.3.4 Volatile Oil

Volatile oils have many common features with gas condensates, but as they contain more heavy compounds they behave liquid-like at reservoir conditions. The phase envelope of a volatile oil is relatively wider than that of a gas condensate, with a higher critical temperature due to its larger concentration of heavy compounds. A typical volatile oil phase diagram is shown in Fig. 2.25.

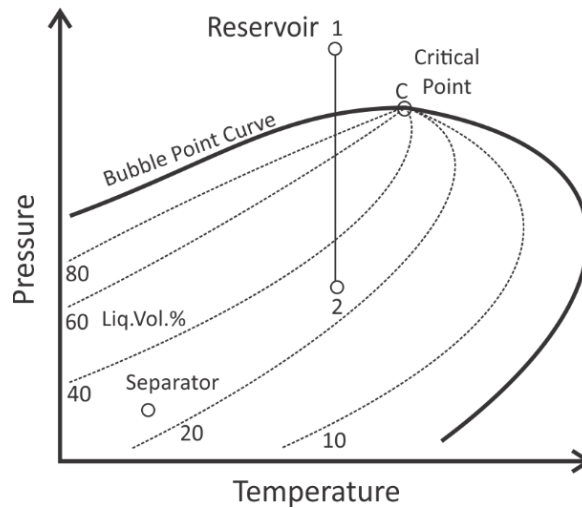


Fig. 2.25. Phase diagram of a volatile oil.

The reservoir temperature is near the critical temperature, hence, volatile oils are referred to as near-critical oils. Note that iso-volume lines are tighter and closer near the bubble point curve. A small reduction of pressure below the bubble point vaporizes a significant fraction of the oil, hence the name "volatile oil". Separator conditions typically lie on low quality (iso-volume) lines.

Initial producing gas to liquid ratios (GOR) of volatile oils typically range between about 310 and 570 v/v (1 750–3 200 SCF/STB) [5]. The GOR increases when the reservoir pressure falls below the bubble point during the reservoir life. The stock tank liquid is colored with a specific gravity usually lower than 0.82 (higher than 40 °API). The specific gravity decreases during production below the bubble point, particularly at high producing GOR, as a significant liquid production is due to condensation of the rich associated gases.

Saturation pressures of volatile oils are high. Gases produced below the bubble point, therefore, are quite rich and behave as retrograde gases. The amount of liquid recovered from the gas constitutes a significant portion of the total oil recovery. Compositional material balance methods should be applied generally to study volatile oil reservoirs.

2.3.5 Black Oil

Black oils, or ordinary oils, are the most common type of oil reserves. The name does not reflect the color, but to distinguish it from the volatile oil. The oil is generally composed of more than about 20 mole% heptanes and heavier compounds (C7+). Its phase envelope, therefore, is the widest of all types of reservoir fluids, with its critical temperature well above the reservoir temperature. A typical black oil phase diagram is shown in Fig. 2.26. The quality lines are broadly spaced at reservoir conditions with separator conditions lying on relatively high quality lines. The above characteristics lead to a low shrinkage of oil when produced.

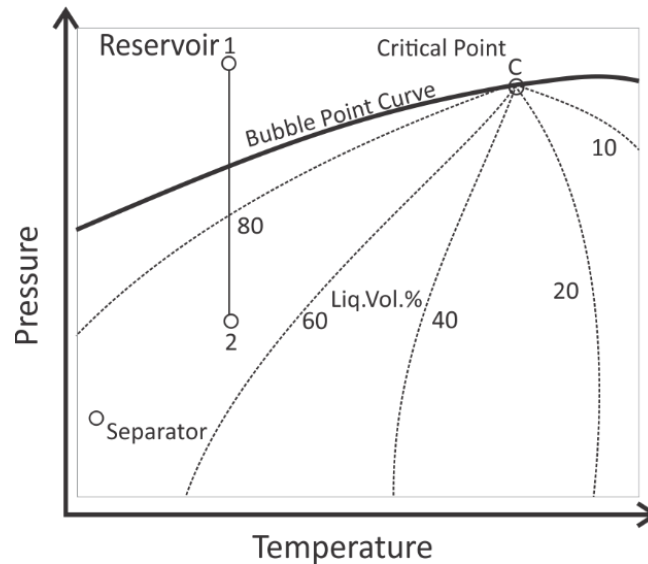


Fig. 2.26. Phase diagram of a black oil.

Initial producing GOR's are less than about 310 v/v (1 750 SCF/STB). The GOR may decrease initially when the reservoir pressure falls below the bubble point, as the evolved gas remains immobile at very low saturations. The GOR, then increases sharply as the gas to oil mobility ratio within the reservoir varies inversely with the viscosity ratio, which is typically of two orders of magnitude. In fractured reservoirs, however, where the fractures provide a good conduit for the gas to rise by gravity, the GOR declines throughout the producing life of the field, as long as the pressure keeps declining and no gas coning takes place. The stock tank liquid is dark with a specific gravity higher than 0.80 (lower than 45 °API) [20]. The variation of the specific gravity is relatively small, in comparison with that of volatile oils, during the reservoir production life.

The saturation pressure of black oils is relatively low. Contribution of heavy compounds present in evolved gases in reservoir to the total liquid recovery is not significant. Hence, volumetric material balance equations, which treat the reservoir fluid as a two component system, i.e., oil and gas, may be sufficient for some reservoir studies. Indeed, as there is no definite boundary between black and volatile oils, the acceptability of results obtained by the volumetric method is a practical criterion for distinguishing between the two types.

2.4 Supercritical fluid

Injection fluids for reservoirs could have supercritical behavior at injection/reservoir conditions.

A supercritical fluid (SCF) is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned".

Supercritical fluids occur in the atmospheres of the gas giants Jupiter and Saturn, and probably in those of the ice giants Uranus and Neptune. In a range of industrial and laboratory processes, they are used as a substitute for organic solvents. Carbon dioxide and water are the most commonly used supercritical fluids, being used for decaffeination and power generation, respectively.

2.4.1 Physio-chemical properties of the supercritical fluids (SCF)

A pure supercritical fluid (SCF) is any compound at a temperature and pressure above the critical values (above critical point). Above the critical temperature of a compound the pure, gaseous component cannot be liquefied regardless of the pressure applied. The critical pressure is the vapor pressure of the gas at the critical temperature. In the supercritical environment only one phase exists. The fluid, as it is termed, is neither a gas nor a liquid and is best described as intermediate to the two extremes. This phase retains solvent power approximating liquids as well as the transport properties common to gases. A comparison of typical values for density, viscosity and diffusivity of gases, liquids, and SCFs is presented in Tbl. 2.5.

Tbl. 2.5. Comparison of physical and transport properties of gases, liquids, and Supercritical Fluids (SCF).

Fluid type	Density (kg/m ³)	Viscosity (mPa s)	Diffusivity (mm ² /s)
Gas	1	0.01	1-10
SCF	100-800	0.05-0.1	0.01-0.1
Liquid	1000	0.5-1.0	0,001

The critical point (C) is marked at the end of the gas-liquid equilibrium curve, and the CO₂ (SC) area indicates the supercritical fluid region, fig. 2.27. It can be shown that by using a combination of isobaric changes in temperature with isothermal changes in pressure, it is possible to convert a pure component from a liquid to a gas (and vice versa) via the supercritical region without incurring a phase transition.

The behavior of a fluid in the supercritical state can be described as that of a very mobile liquid. The solubility behavior approaches that of the liquid phase while penetration into a solid matrix is facilitated by the gas-like transport properties. As a consequence, the rates of extraction and phase separation can be significantly faster than for conventional extraction processes. Furthermore, the extraction conditions can be controlled to affect a selected separation. Supercritical fluid extraction is known to be dependent on the density of the fluid that in turn can be manipulated through control of the system pressure and temperature. The dissolving power of a SCF increases with isothermal increase in density or an isopycnic (i.e. constant density) increase in temperature. In practical terms this means a SCF can be used to extract a solute from a feed matrix as in conventional liquid extraction. However, unlike conventional extraction, once the conditions are returned to ambient the quantity of residual solvent in the extracted material is negligible.

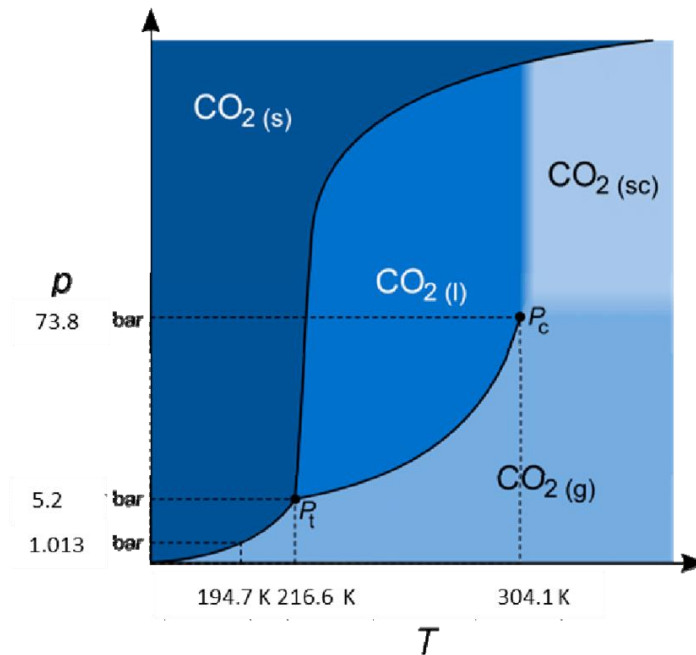


Fig. 2.27. Carbon dioxide (CO₂) pressure–temperature phase diagram

The basic principle of SCF extraction is that the solubility of a given compound (solute) in a solvent varies with both temperature and pressure. At ambient conditions (25°C and 1 bar) the solubility of a solute in a gas is usually related directly to the vapor pressure of the solute and is generally negligible. In a SCF, however, solute solubilities of up to 10 orders of magnitude greater than those predicted by ideal gas law behavior have been reported.

The dissolution of solutes in supercritical fluids results from a combination of vapor pressure and solute-solvent interaction effects. The impact of this is that the solubility of a solid solute in a supercritical fluid is not a simple function of pressure.

Although the solubility of volatile solids in SCFs is higher than in an ideal gas, it is often desirable to increase the solubility further in order to reduce the solvent requirement for processing. The solubility of components in SCFs can be enhanced by the addition of a substance referred to as an entrainer, or cosolvent. The volatility of this additional component is usually intermediate to that of the SCF and the solute. The addition of a cosolvent provides a further dimension to the range of solvent properties in a given system by influencing the chemical nature of the fluid.

Cosolvents also provide a mechanism by which the extraction selectivity can be manipulated. The commercial potential of a particular application of SCF technology can be significantly improved through the use of cosolvents. A factor that must be taken into consideration when using cosolvents, however, is that even the presence of small amounts of an additional component to a primary SCF can change the critical properties of the resulting mixture considerably.

In general terms, supercritical fluids have properties between those of a gas and a liquid. In Tbl. 2.6, the critical properties are shown for some substances that are commonly used as supercritical fluids.

In addition, there is no surface tension in a supercritical fluid, as there is no liquid/gas phase boundary. By changing the pressure and temperature of the fluid, the properties can be "tuned" to be more liquid-like or more gas-like.

One of the most important properties is the solubility of material in the fluid. Solubility in a supercritical fluid tends to increase with density of the fluid (at constant temperature). Since density increases with pressure, solubility tends to increase with pressure. The relationship with temperature is a little more

complicated. At constant density, solubility will increase with temperature. However, close to the critical point, the density can drop sharply with a slight increase in temperature. Therefore, close to the critical temperature, solubility often drops with increasing temperature, then rises again.

Carbon dioxide (CO₂) is the most commonly used SCF, due primarily to its low critical parameters (31.1°C, 73.8 bar), low cost and non-toxicity. However, several other SCFs have been used in both commercial and development processes.

Tbl. 2.6. Critical properties of various solvents.

Solvent	M g/mol	T _c K	P _c MPa (atm)	ρ _c g/cm ³
Carbon dioxide (CO ₂)	44.01	304.1	7.38 (72.8)	0.469
Water (H ₂ O)	18.015	647.096	22.06 (217.76)	0.322
Methane (CH ₄)	16.04	190.4	4.60 (45.4)	0.162
Ethane (C ₂ H ₆)	30.07	305.3	4.87 (48.1)	0.203
Propane (C ₃ H ₈)	44.09	369.8	4.25 (41.9)	0.217
n-butane	58.12	425.16	3.796	0.225
n-pentane	72.15	469.6	3.369	0.273
cyclohexane	84.16	553.5	4.07	0.322
toluene	92.14	591.8	4.13	0.316
Ethylene (C ₂ H ₄)	28.05	282.4	5.04 (49.7)	0.215
Propylene (C ₃ H ₆)	42.08	364.9	4.60 (45.4)	0.232
Methanol (CH ₃ OH)	32.04	512.6	8.09 (79.8)	0.272
Ethanol (C ₂ H ₅ OH)	46.07	513.9	6.14 (60.6)	0.276
Acetone (C ₃ H ₆ O)	58.08	508.1	4.70 (46.4)	0.278
Nitrous oxide (N ₂ O)	44.013	306.57	7.35 (72.5)	0.452
Ammonia (NH ₃)	17.03	405.5	11.28	0.243
Trifluoromethane (Fluoroform)		299.3	48.6 bar	
Chlorotrifluoromethane		302.0	38.7 bar	
Trichlorofluoromethane		471.2	44.1 bar	

Fig. 2.27 and 2.28 show two-dimensional projections of a phase diagram for CO₂. In the pressure-temperature phase diagram (Fig. 1) the boiling separates the gas and liquid region and ends in the critical point, where the liquid and gas phases disappear to become a single supercritical phase.

The appearance of a single phase can also be observed in the density-pressure phase diagram for carbon dioxide (Fig. 2.28). At well below the critical temperature, e.g., 280K, as the pressure increases, the gas compresses and eventually (at just over 40 bar) condenses into a much denser liquid, resulting in the discontinuity in the line (vertical dotted line). The system consists of 2 phases in equilibrium, a dense liquid and a low density gas. As the critical temperature is approached (300K), the density of the gas at equilibrium becomes higher, and that of the liquid lower. At the critical point, (304.1 K and 7.38 MPa (73.8 bar)), there is no difference in density, and the 2 phases become one fluid phase. Thus, above the critical temperature a gas cannot be liquefied by pressure. At slightly above the critical temperature (310K), in the vicinity of the critical pressure, the line is almost vertical. A small increase in pressure causes a large increase in the density of the supercritical phase. Many other physical properties also show large gradients with pressure near the critical point, e.g. viscosity, the relative

permittivity and the solvent strength, which are all closely related to the density. At higher temperatures, the fluid starts to behave like a gas, as can be seen in Fig. 2.28. For carbon dioxide at 400 K, the density increases almost linearly with pressure.

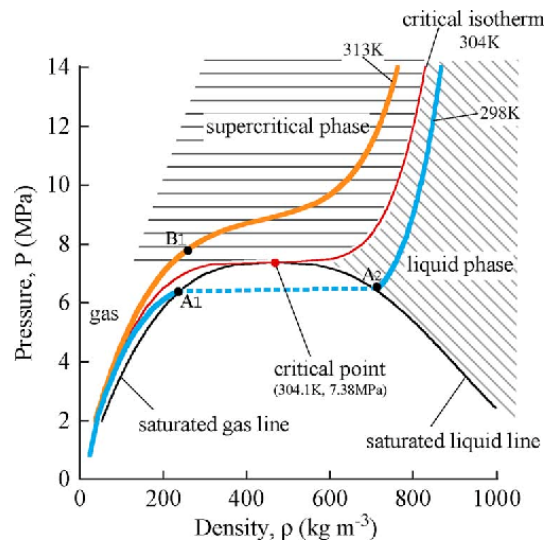


Fig. 2.28. Carbon dioxide (CO₂) pressure–density phase diagram

Many pressurized gases are actually supercritical fluids. For example, nitrogen has a critical point of 126.2 K (–147 °C) and 3.4 MPa (34 bar). Therefore, nitrogen (or compressed air) in a gas cylinder above this pressure is actually a supercritical fluid. These are more often known as permanent gases. At room temperature, they are well above their critical temperature, and therefore behave as a gas, similar to CO₂ at 400 K above. However, they cannot be liquified by pressure unless cooled below their critical temperature.

2.4.2 Mixtures

Typically, supercritical fluids are completely miscible with each other, so that a binary mixture forms a single gaseous phase if the critical point of the mixture is exceeded. However, exceptions are known in systems where one component is much more volatile than the other, which in some cases form two immiscible gas phases at high pressure and temperatures above the component critical points. This behavior has been found for example in the systems N₂–NH₃, NH₃–CH₄, SO₂–N₂ and n–butane–H₂O [4]. The critical point of a binary mixture can be estimated as the arithmetic mean of the critical temperatures and pressures of the two components A and B, eq. 2.18.

$$T_{c(\text{mix})} = (\text{mole fraction})_A \cdot T_{cA} + (\text{mole fraction})_B \cdot T_{cB} \quad 2.18$$

For greater accuracy, the critical point can be calculated using equations of state, such as the Peng Robinson, or group contribution methods. Other properties, such as density, can also be calculated using equations of state [24].

2.4.3 Thermodynamics

A significant effort has been devoted to investigation of various properties of supercritical fluids. This has been an exciting field with a long history since 1822 when Baron Charles Cagniard de la Tour discovered supercritical fluids while conducting experiments involving the discontinuities of the sound in a sealed cannon barrel filled with various fluids at high temperature. More recently, supercritical fluids have found application in a variety of fields, ranging from the extraction of floral fragrance from

flowers to applications in food science such as creating decaffeinated coffee, functional food ingredients, pharmaceuticals, cosmetics, polymers, powders, bio- and functional materials, nano-systems, natural products, biotechnology, fossil and bio-fuels, microelectronics, energy and environment. Much of the excitement and interest of the past decade is due to the enormous progress made in increasing the power of relevant experimental tools. The development of new experimental methods and improvement of existing ones continues to play an important role in this field, with recent research focusing on dynamic properties of fluids.

The Fisher–Widom line, the Widom line, or the Frenkel line are thermodynamic concepts that allow to distinguish liquid-like and gas-like states within the supercritical fluid.

2.4.4 Natural occurrence

Hydrothermal circulation occurs within the Earth's crust wherever fluid becomes heated and begins to convect. These fluids are thought to reach supercritical conditions under a number of different settings, such as in the formation of porphyry copper deposits or high temperature circulation of seawater in the sea floor. At mid-ocean ridges, this circulation is most evident by the appearance of hydrothermal vents known as "black smokers". These are large (meters high) chimneys of sulfide and sulfate minerals which vent fluids up to 400 °C. The fluids appear like great black billowing clouds of smoke due to the precipitation of dissolved metals in the fluid. It is likely that at depth many of these vent sites reach supercritical conditions, but most cool sufficiently by the time they reach the sea floor to be subcritical. One particular vent site, Turtle Pits, has displayed a brief period of supercriticality at the vent site. A further site, Beebe, in the Cayman Trough, is thought to display sustained supercriticality at the vent orifice. [25]

2.4.5 Planetary atmospheres

The atmosphere of Venus is 96.5% carbon dioxide and 3.5% nitrogen. The surface pressure is 9.3 MPa (93 bar) and the surface temperature is 735 K, above the critical points of both major constituents and making the surface atmosphere a supercritical fluid.

The interior atmospheres of the solar system's gas giant planets are composed mainly of hydrogen and helium at temperatures well above their critical points. The gaseous outer atmospheres of Jupiter and Saturn transition smoothly into the dense liquid interior, while the nature of the transition zones of Neptune and Uranus is unknown. Theoretical models of extrasolar planets 55 Cancri e and Gliese 876 d have posited an ocean of pressurized, supercritical fluid water with a sheet of solid high pressure water ice at the bottom.

2.4.6 Applications of supercritical fluids (SCF)

History

In 1822, Baron Charles Cagniard de la Tour discovered the critical point of a substance in his famous cannon barrel experiments. Listening to discontinuities in the sound of a rolling flint ball in a sealed cannon filled with fluids at various temperatures, he observed the critical temperature. Above this temperature, the densities of the liquid and gas phases become equal and the distinction between them disappears, resulting in a single supercritical fluid phase.[26]

Enhanced oil recovery and carbon capture and storage

Supercritical carbon dioxide is used to enhance oil recovery in mature oil fields. At the same time, there is the possibility of using "clean coal technology" to combine enhanced recovery methods with carbon sequestration. The CO₂ is separated from other flue gases, compressed to the supercritical state, and injected into geological storage, possibly into existing oil fields to improve yields.

At present, only schemes isolating fossil CO₂ from natural gas actually use carbon storage, (e.g., Sleipner gas field),[27] but there are many plans for future CCS schemes involving pre- or post-combustion CO₂. [28][29][30][31] There is also the possibility to reduce the amount of CO₂ in the atmosphere by using biomass to generate power and sequestering the CO₂ produced.

Enhanced geothermal system

The use of supercritical carbon dioxide, instead of water, has been examined as a geothermal working fluid.

Supercritical fluid in power generation

The efficiency of a heat engine is ultimately dependent on the temperature difference between heat source and sink (Carnot cycle). To improve efficiency of power stations the operating temperature must be raised. Using water as the working fluid, this takes it into supercritical conditions.[32] Efficiencies can be raised from about 39% for subcritical operation to about 45% using current technology.[33] Supercritical water reactors (SCWRs) are promising advanced nuclear systems that offer similar thermal efficiency gains. Carbon dioxide can also be used in supercritical cycle nuclear power plants, with similar efficiency gains.[34] Many coal-fired supercritical steam generators are operational all over the world, and have enhanced the efficiency of traditional steam-power plants.

Refrigeration

Supercritical carbon dioxide is also an important emerging refrigerant, being used in new, low-carbon solutions for domestic heat pumps.[35] These systems are undergoing continuous development with supercritical carbon dioxide heat pumps already being successfully marketed in Asia. The EcoCute systems from Japan, developed by consortium of companies including Mitsubishi, develop high-temperature domestic water with small inputs of electric power by moving heat into the system from their surroundings. Their success makes a future use in other world regions possible.[36]

Biodiesel production

Conversion of vegetable oil to biodiesel is via a transesterification reaction, where the triglyceride is converted to the methyl ester plus glycerol. This is usually done using methanol and caustic or acid catalysts but can be achieved using supercritical methanol without a catalyst. The method of using supercritical methanol for biodiesel production was first studied by Saka and his coworkers. This has the advantage of allowing a greater range and water content of feedstocks (in particular, used cooking oil), the product does not need to be washed to remove catalyst, and is easier to design as a continuous process.[37]

Supercritical water hydrolysis

Supercritical hydrolysis is a method of converting all biomass polysaccharides as well the associated lignin into low molecular compounds by contacting with water alone under supercritical conditions. The supercritical water, acts as a solvent, a supplier of bond-breaking thermal energy, a heat transfer agent and as a source of hydrogen atoms. All polysaccharides are converted into simple sugars in near-quantitative yield in a second or less. The aliphatic inter-ring linkages of lignin are also readily cleaved into free radicals that are stabilized by hydrogen originating from the water. The aromatic rings of the lignin are unaffected under short reaction times so that the lignin-derived products are low molecular weight mixed phenols. To take advantage of the very short reaction times needed for cleavage a continuous reaction system must be devised. The amount of water heated to a supercritical state is thereby minimized.

Supercritical water gasification

Supercritical water gasification is a process of exploiting the beneficial effect of supercritical water to convert aqueous biomass streams into clean water and gases like H₂, CH₄, CO₂, CO etc. [38]

Supercritical water oxidation

Supercritical water oxidation uses supercritical water as a medium in which to oxidize hazardous waste, eliminating production of toxic combustion products that burning can produce.

The waste product to be oxidised is dissolved in the supercritical water along with molecular oxygen (or an oxidising agent that gives up oxygen upon decomposition, e.g. hydrogen peroxide) at which point the oxidation reaction occurs.[39]

2.4.7 Application of supercritical fluid extraction (SFE)

The choice of the SFE solvent is similar to the regular extraction. Principle considerations are the followings.

- * Good solvency property
- * Inert to the product
- * Easy separation from the product
- * Cheap
- * Low P_c because of economic reasons

Supercritical extraction is not widely used yet, but as new technologies are coming there are more and more viewpoints that could justify it, as high purity, residual solvent content, environment protection.

Supercritical fluid extraction

The advantages of supercritical fluid extraction (compared with liquid extraction) are that it is relatively rapid because of the low viscosities and high diffusivities associated with supercritical fluids. The extraction can be selective to some extent by controlling the density of the medium, and the extracted material is easily recovered by simply depressurizing, allowing the supercritical fluid to return to gas phase and evaporate. The extracted component is then separated from the SCF. The SCF is then recompressed to the extraction conditions and recycled.

Carbon dioxide is the most common supercritical solvent. It is used on a large scale for the decaffeination of green coffee beans, the extraction of hops for beer production,[40] and the production of essential oils and pharmaceutical products from plants.[41] A few laboratory test methods include the use of supercritical fluid extraction as an extraction method instead of using traditional solvents.[42][43][44]

Some of the advantages and disadvantages of SCFs compared to conventional liquid solvents for separations:

Advantages

- * Dissolving power of the SCF is controlled by pressure and/or temperature
- * SCF is easily recoverable from the extract due to its volatility
- * Non-toxic solvents leave no harmful residue
- * High boiling components are extracted at relatively low temperatures
- * Separations not possible by more traditional processes can sometimes be effected
- * Thermally labile compounds can be extracted with minimal damage as low temperatures can be employed by the extraction

Disadvantages

- * Elevated pressure required
- * Compression of solvent requires elaborate recycling measures to reduce energy costs
- * High capital investment for equipment

2.4.8 Other proposed applications of SCF

Supercritical fluid decomposition

Supercritical water can be used to decompose biomass via supercritical water gasification of biomass.[45] This type of biomass gasification can be used to produce hydrocarbon fuels for use in an efficient combustion device or to produce hydrogen for use in a fuel cell. In the latter case, hydrogen yield can be much higher than the hydrogen content of the biomass due to steam reforming where water is a hydrogen-providing participant in the overall reaction.

Dry-cleaning

Supercritical carbon dioxide (SCD) can be used instead of PERC (perchloroethylene) or other undesirable solvents for dry-cleaning. Supercritical carbon dioxide sometimes intercalates into buttons, and, when the SCD is depressurized, the buttons pop, or break apart. Detergents that are soluble in carbon dioxide improve the solvating power of the solvent.[46]

Supercritical fluid chromatography

Supercritical fluid chromatography (SFC) can be used on an analytical scale, where it combines many of the advantages of high performance liquid chromatography (HPLC) and gas chromatography (GC). It can be used with non-volatile and thermally labile analytes (unlike GC) and can be used with the universal flame ionization detector (unlike HPLC), as well as producing narrower peaks due to rapid diffusion. In practice, the advantages offered by SFC have not been sufficient to displace the widely used HPLC and GC, except in a few cases such as chiral separations and analysis of high-molecular-weight hydrocarbons.[47] For manufacturing, efficient preparative simulated moving bed units are available.[48] The purity of the final products is very high, but the cost makes it suitable only for very high-value materials such as pharmaceuticals.

Chemical reactions

Changing the conditions of the reaction solvent can allow separation of phases for product removal, or single phase for reaction. Rapid diffusion accelerates diffusion controlled reactions. Temperature and pressure can tune the reaction down preferred pathways, e.g., to improve yield of a particular chiral isomer.[49] There are also significant environmental benefits over conventional organic solvents. An electrochemical carboxylation of a para-isobutylbenzyl chloride to Ibuprofen is promoted under supercritical carbon dioxide.[50]

Impregnation and dyeing

Impregnation is, in essence, the converse of extraction. A substance is dissolved in the supercritical fluid, the solution flowed past a solid substrate, and is deposited on or dissolves in the substrate. Dyeing, which is readily carried out on polymer fibres such as polyester using disperse (non-ionic) dyes, is a special case of this. Carbon dioxide also dissolves in many polymers, considerably swelling and plasticising them and further accelerating the diffusion process.

Nano and micro particle formation

See also: micronization

The formation of small particles of a substance with a narrow size distribution is an important process in the pharmaceutical and other industries. Supercritical fluids provide a number of ways of achieving this by rapidly exceeding the saturation point of a solute by dilution, depressurization or a combination of these. These processes occur faster in supercritical fluids than in liquids, promoting nucleation or spinodal decomposition over crystal growth and yielding very small and regularly sized particles. Recent supercritical fluids have shown the capability to reduce particles up to a range of 5–2000 nm.[51]

Generation of pharmaceutical cocrystals

Supercritical fluids act as a new media for the generation of novel crystalline forms of APIs (Active Pharmaceutical Ingredients) named as pharmaceutical cocrystals. Supercritical fluid technology offers a new platform that allows a single-step generation of particles that are difficult or even impossible to obtain by traditional techniques. The generation of pure and dried new cocrystals (crystalline molecular complexes comprising the API and one or more conformers in the crystal lattice) can be achieved due to unique properties of SCFs by using different supercritical fluid properties: supercritical CO₂ solvent power, anti-solvent effect and its atomization enhancement.[52][53]

Supercritical drying

See also: Critical point drying

Supercritical drying is a method of removing solvent without surface tension effects. As a liquid dries, the surface tension drags on small structures within a solid, causing distortion and shrinkage. Under supercritical conditions there is no surface tension, and the supercritical fluid can be removed without distortion. Supercritical drying is used for manufacture of aerogels and drying of delicate materials such as archeological samples and biological samples for electron microscopy. Carbon dioxide is used as a supercritical solvent in some dry cleaning processes.

Supercritical fluid deposition

Supercritical fluids can be used to deposit functional nanostructured films and nanometer-size particles of metals onto surfaces. The high diffusivities and concentrations of precursor in the fluid as compared to the vacuum systems used in chemical vapour deposition allow deposition to occur in a surface reaction rate limited regime, providing stable and uniform interfacial growth.[54] This is crucial in developing more powerful electronic components, and metal particles deposited in this way are also powerful catalysts for chemical synthesis and electrochemical reactions. Additionally, due to the high rates of precursor transport in solution, it is possible to coat high surface area particles which under chemical vapour deposition would exhibit depletion near the outlet of the system and also be likely to result in unstable interfacial growth features such as dendrites. The result is very thin and uniform films deposited at rates much faster than atomic layer deposition, the best other tool for particle coating at this size scale.[55]

Antimicrobial properties

CO₂ at high pressures has antimicrobial properties.[56] While its effectiveness has been shown for various applications, the mechanisms of inactivation have not been fully understood although they have been investigated for more than 60 years.[57]

REFERENCES

1. Hunt, J.A.M: "Petroleum Geochemistry and Geology", W.H. Freeman and Co., San Francisco (1979).
2. England, W.A. and Mackenzie, A.S: "Geochemistry of Petroleum Reservoirs", *Geologische Rundschau*, 78, 214–237(1989).
3. Nelson, W.L.: "Petroleum Refinery Engineering", 4th Ed., McGraw–Hill, New York (1958).
4. Institute of Petroleum:" Methods for Analysis and Testing ",The Institute of Petroleum, John Wiley and Sons, New York (1984).
5. McCain, W.D: "The Properties of Petroleum Fluids", 2nd Ed., Pennwell Books, Tulsa (1990).
6. Sachanen, A.N: "The Chemical Constituents of Petroleum", Reinhold Pub. Co. (1945).
7. Larter, S.R., and Aplin, A.C:"Reservoir Geochemistry: Methods, Applications and Opportunities" In: England, W.A. and Cubitt, J. (eds) 'The Geochemistry of Reservoirs" *Geol. Soc. Publication* (1994).
8. Katz, D. et al:" Handbook of Natural Gas Engineering ", McGraw–Hill Book Company (1959).
9. Gas Processors Suppliers Association, ed.: "SI Engineering Data Book", Tulsa, Oklahoma (1980).
10. Brown G.G., Katz D.L., Oberfell G.G. and Alden R.C:"Natural Gasoline and the Volatile Hydrocarbons", *NGA of America*, Tulsa, (1948).
11. Pitzer, K.S., Lippmann D.Z., Curl, R.F. Jr., Huggins C.M. and Petersen, D.E: "The Volumetric and Thermodynamic Properties of Fluids. II. Compressibility Factors, Vapor Pressure and Entropy of Vaporisation." *J. of the American Chemical Society*, 77, 3433–3440, (July 5, 1955).
12. Lee, B.I. and Kesler, MG:"A Generalised Thermodynamics Correlation Based on Three–Parameter Corresponding States", *AIChE J.*,21 No.4, 510–527 (May, 1975).
13. Rackett, H.G:"Equation of State for Saturated Liquids", *J. Chem. Eng. Data*, 15 No.4, 514–517, (1973).
14. Spencer, C.F. and Banner, R.P: "Prediction of Bubble Point Pressure of Mixtures", *J. Chem. Eng. Data*, 18, No.2, 230–234, (1973).
15. Spencer, C.F. and Adler, S.B:"A Critical Review of Equations for Predicting Saturated Liquid Density", *J. Chem. Eng. Data*, Vol. 23, No. 1, 82–89 (1978).
16. Yamada,T. and Gunn, R:"Saturated Liquid Molar Volumes: the Rackett Equation", *J.Chem. Eng.,Data*, 18 No.2, 234–236 (1973).
17. Weinaug, C.F. and Bradley, H.B: "Phase Behaviour of a Natural Hydrocarbon System", *Trans. AIME*, 192, 233 (1951).
18. Danesh , A., Xu, D., and Todd A.C: " An Evaluation of Cubic Equation of State for Phase Behaviour Calculations Near Miscibility Conditions ", *SPE/DOE 20267*, Paper Presented at the Seventh Symposium on Enhanced Oil Recovery, Tulsa, Oklahoma, April 22–25 (1990).
19. McCain Jr, W.D., and Bridges B: "Volatile Oils and Retrograde Gases. What's the Difference?", *Petroleum Engineer International*, 35–36 (Jan., 1994).
20. Moses, P.L: "Engineering Applications of Phase Behaviour of Crude Oil and Condensate Systems", *JPT*, 715–723 (July, 1986).
21. Kilgren, K.H: "Phase Behaviour of a High–Pressure Condensate Reservoir Fluid", *JPT*, 1001–1005 (Aug., 1966).
22. Danesh, A., Henderson, G.D. and Peden, J.M: "Experimental Investigation of Critical Condensate Saturation and its Dependence on Connate Water Saturation", *SPE Res. Eng. Journal*, 336–342 (Aug., 1991).
23. "Supercritical Fluid Extraction, Density Considerations". Retrieved 2007-11-20.
24. Gordon, R. P. (1972). "A Supercritical Phase Separation". *Journal of Chemical Education*. 49 (4): 249–252. doi:10.1021/ed049p249.
25. A. A. Clifford (2007-12-04). "Calculation of Thermodynamic Properties of CO2 using Peng–Robinson equation of state". *Critical Processes Ltd*. Archived from the original on 2008-05-05. Retrieved 2007-11-20.

26. Berche, Bertrand; Henkel, Malte; Kenna, Ralph (2009). "Critical phenomena: 150 years since Cagniard de la Tour". *Journal of Physical Studies*. 13 (3): 3001–1–3001–4. arXiv:0905.1886. Bibcode:2009arXiv0905.1886B. doi:10.1590/S1806-11172009000200015.
27. "Saline Aquifer CO2 Storage". Retrieved 2007-12-10.
28. "The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs", p. 84 (2004)
29. FutureGen Technology Archived 2008-01-01 at the Wayback Machine
30. Øyvind Vessia: "Fischer- Tropsch reactor fed by syngas" Archived 2007-09-29 at the Wayback Machine
31. Intergovernmental Panel on Climate Change IPCC Special Report on Carbon Dioxide Capture and Storage.
32. Malhotra, Ashok and Satyakam,R, 2000,Influence of climatic parameters on optimal design of supercritical power plants,IECEC, Energy Conversion Engineering Conference, pp. 1053–1058,
33. "Supercritical steam cycles for power generation applications" (PDF). Archived from the original (PDF) on December 17, 2008. Retrieved 2007-11-20.
34. V. Dostal; M.J. Driscoll; P. Hejzlar. "A Supercritical Carbon Dioxide Cycle for Next Generation Nuclear Reactors" (PDF). MIT-ANP-TR-100. MIT-ANP-Series. Retrieved 2007-11-20.
35. FAQs – Supercritical CO2 in heat pumps and other applications Archived 2007-10-06 at the Wayback Machine
36. Ye, Xiang-Rong; Lin, YH & Wai, CM (2003). "Supercritical fluid fabrication of metal nanowires and nanorods templated by multiwalled carbon nanotubes". *Advanced Materials*. 15 (4): 316–319. doi:10.1002/adma.200390077.
37. Kunchana Bunyakiat; Sukunya Makmee; Ruengwit Sawangkeaw & Somkiat Ngamprasertsith (2006). "Continuous Production of Biodiesel via Transesterification from Vegetable Oils in Supercritical Methanol". *Energy and Fuels*. 20 (2): 812–817. doi:10.1021/ef050329b.
38. "Reforming in supercritical water". Retrieved 16 May 2017.
39. Padrela, Luis (2010). "Screening for pharmaceutical cocrystals using the supercritical fluid enhanced atomization process". *The Journal of Supercritical Fluids*. 53 (1–3): 156–164. doi:10.1016/j.supflu.2010.01.010.
40. Webber, A.P.; Murton, B.; Roberts, S.; Hodgkinson, M. "Supercritical Venting and VMS Formation at the Beebe Hydrothermal Field, Cayman Spreading Centre". *Goldschmidt Conference Abstracts 2014*. Geochemical Society. Archived from the original on 29 July 2014. Retrieved 29 July 2014.
41. "The Naked Scientist Interviews". 15 July 2007. Retrieved 2007-11-20.
42. Aizpurua-Olaizola, Oier; Ormazabal, Markel; Vallejo, Asier; Olivares, Maitane; Navarro, Patricia; Etxebarria, Nestor; Usobiaga, Aresatz (2015-01-01). "Optimization of Supercritical Fluid Consecutive Extractions of Fatty Acids and Polyphenols from Vitis Vinifera Grape Wastes". *Journal of Food Science*. 80 (1): E101–E107. doi:10.1111/1750-3841.12715. ISSN 1750-3841. PMID 25471637.
43. U.S.EPA Method 3560 Supercritical Fluid Extraction of Total Recoverable Hydrocarbons. <https://www.epa.gov/sites/production/files/2015-12/documents/3560.pdf>
44. U.S.EPA Method 3561 Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons. <https://www.epa.gov/sites/production/files/2015-12/documents/3561.pdf>
45. Use of Ozone Depleting Substances in Laboratories. TemaNord 2003:516. "Archived copy" (PDF). Archived from the original (PDF) on 2008-02-27. Retrieved 2011-03-28.
46. "Supercritical water gasification of biomass". Archived from the original on 2009-03-23. Retrieved 2011-11-17.
47. "Science News Online". Retrieved 2007-11-20.
48. Bart, C. J. (2005). "Chapter 4: Separation Techniques". *Additives in Polymers: industrial analysis and applications*. John Wiley and Sons. p. 212. doi:10.1002/0470012064.ch4. ISBN 978-0-470-01206-2.
49. "Simulated Moving Bed Theory" (PDF). Archived from the original (PDF) on 2004-08-29. Retrieved 2007-11-20.
50. R. Scott Oakes; Anthony A. Clifford; Keith D. Bartle; Mark Thornton Pett & Christopher M. Rayner (1999). "Sulfur oxidation in supercritical carbon dioxide: dramatic pressure dependent enhancement of

- diastereoselectivity for sulphoxidation of cysteine derivatives". *Chemical Communications*. 44 (3): 247–248. doi:10.1039/a809434i.
51. Sakakura, Toshiyasu; Choi, Jun-Chul; Yasuda, Hiroyuki (13 June 2007). "Transformation of Carbon dioxide". *Chemical Reviews*. 107 (6): 2365–2387. doi:10.1021/cr068357u. PMID 17564481.
 52. Padrela, L.; Rodrigues, M.A.; Velaga, S.P.; Matos, H.A.; Azevedo, E.G. (2009). "Formation of indomethacin–saccharin cocrystals using supercritical fluid technology". *European Journal of Pharmaceutical Sciences*. 38 (1): 9–17. doi:10.1016/j.ejps.2009.05.010. PMID 19477273.
 53. Sang-Do Yeo & Erdogan Kiran (2005). "Formation of polymer particles with supercritical fluids: A review". *The Journal of Supercritical Fluids*. 34 (3): 287–308. doi:10.1016/j.supflu.2004.10.006.
 54. "SFD compared to CVD". *navolta.com*. Navolta. Archived from the original on 5 October 2014. Retrieved 3 October 2014.
 55. Cinquemani, C; Boyle, C; Bach, E & Schollmeyer, E (2007). "Inactivation of microbes using compressed carbon dioxide - An environmentally sound disinfection process for medical fabrics". *Journal of Supercritical Fluids*. 42 (3): 392–397. doi:10.1016/j.supflu.2006.11.001.
 56. Fraser, D (1951). "Bursting bacteria by release of gas pressure". *Nature*. 167 (4236): 33–34. Bibcode:1951Natur.167...33F. doi:10.1038/167033b0. PMID 14796728.
 57. Berche, Bertrand; Henkel, Malte; Kenna, Ralph (2009). "Critical phenomena: 150 years since Cagniard de la Tour". *Journal of Physical Studies*. 13 (3): 3001–1–3001–4. arXiv:0905.1886. Bibcode:2009arXiv0905.1886B. doi:10.1590/S1806-11172009000200015.

