Danesh, Ali. ***PVT and phase behaviour of petroleum reservoir fluids*****. Elsevier, 1998.**

فصل اول کتاب دانش را مطالعه کنید.

https://mnlotfollahi.profile.semnan.ac.ir/#about_me

mnlotfollahi@yahoo.com

Home works:

Chapter 1: 1, 2, 3, 4, 5

هر گروه ۲ یا ۳ نفره یک نسخه تحویل دهند.

نکته اول و مهم: اعضای هر گروه تا آخر ترم تغییر نکنند.
نکته دوم: یا حل مسائل در Word تایپ شود وفایل آن ایمیل شود و یا حل مسائل روی کاغذ انجام شود و با CamScanner عکس گرفته شود تا سیاه و سفید بوده و کادر ورق کامل باشد وفایل آن ایمیل شود.

Chapter 1: Phase Behavior Fundamentals

فصل اول:

۱-۱- ترکیب سیال مخزن

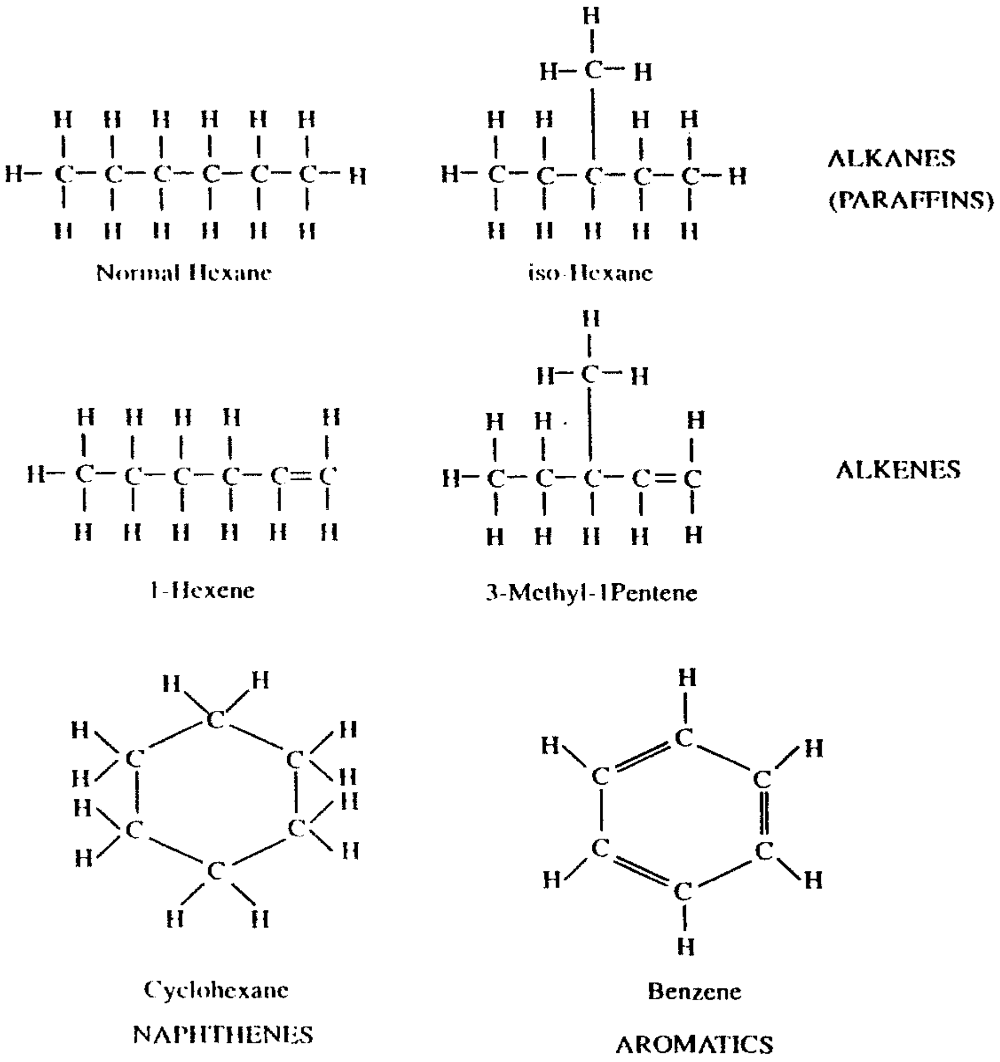
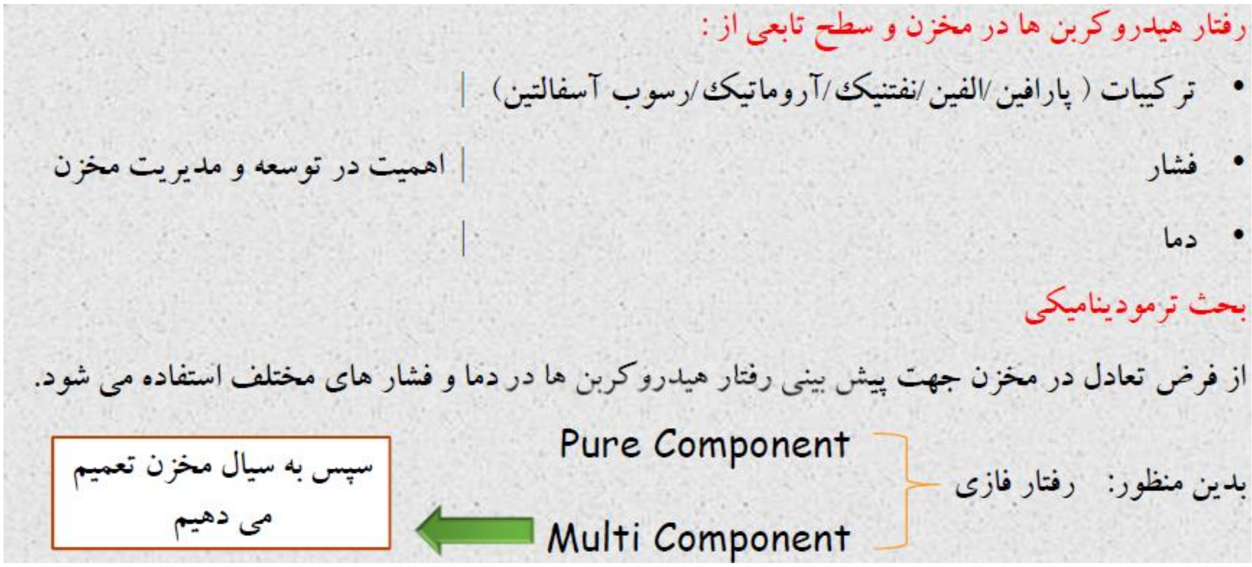


Figure 1.1. Structural formula of various groups of hydrocarbons with six carbons.

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 ξ. 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 C_6-C_{11} 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 Figure 1.1.



رفتار هیدروکربن ها در مخزن و سطح تابعی از:

- ترکیبات (پارافین/الفین/نفتنیک/آروماتیک/رسوب آسفالتین)
- فشار
- دما

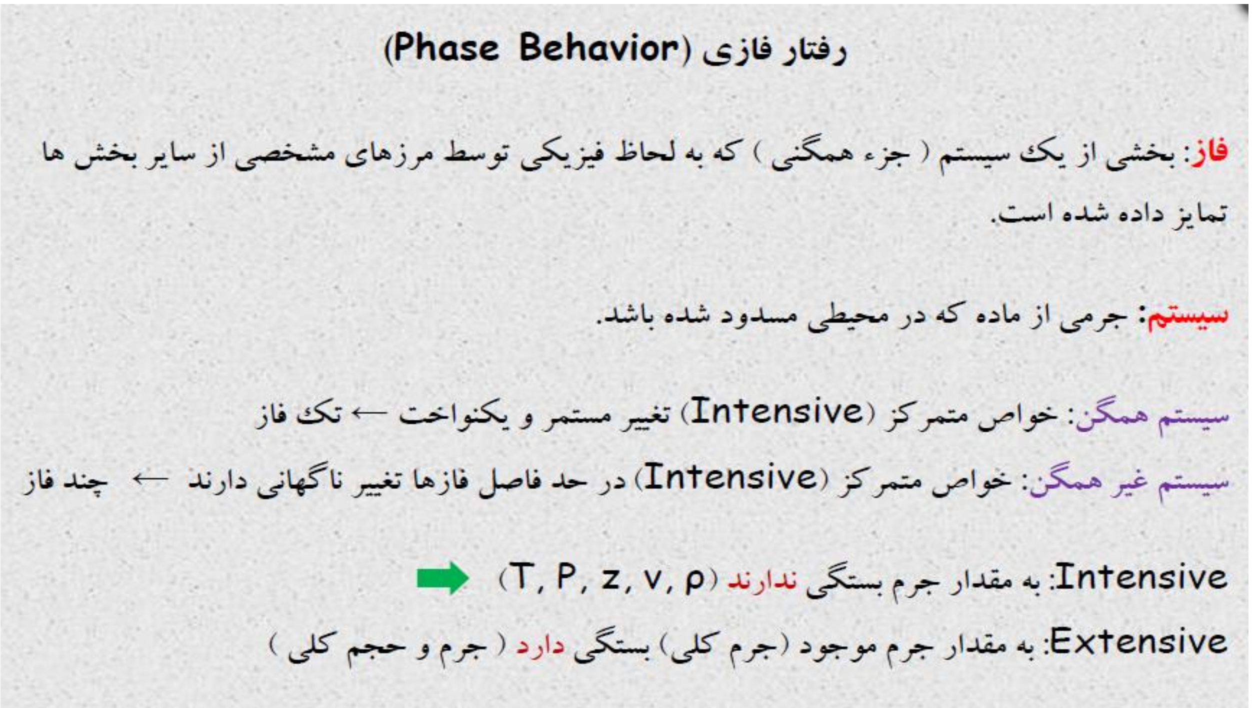
اهمیت در توسعه و مدیریت مخزن

بحث ترمودینامیکی

از فرض تعادل در مخزن جهت پیش بینی رفتار هیدروکربن ها در دما و فشار های مختلف استفاده می شود.

بدین منظور: رفتار فازی
Pure Component
Multi Component

سپس به سیال مخزن تعمیم می دهیم



رفتار فازی (Phase Behavior)

فاز: بخشی از یک سیستم (جزء همگنی) که به لحاظ فیزیکی توسط مرزهای مشخصی از سایر بخش ها تمایز داده شده است.

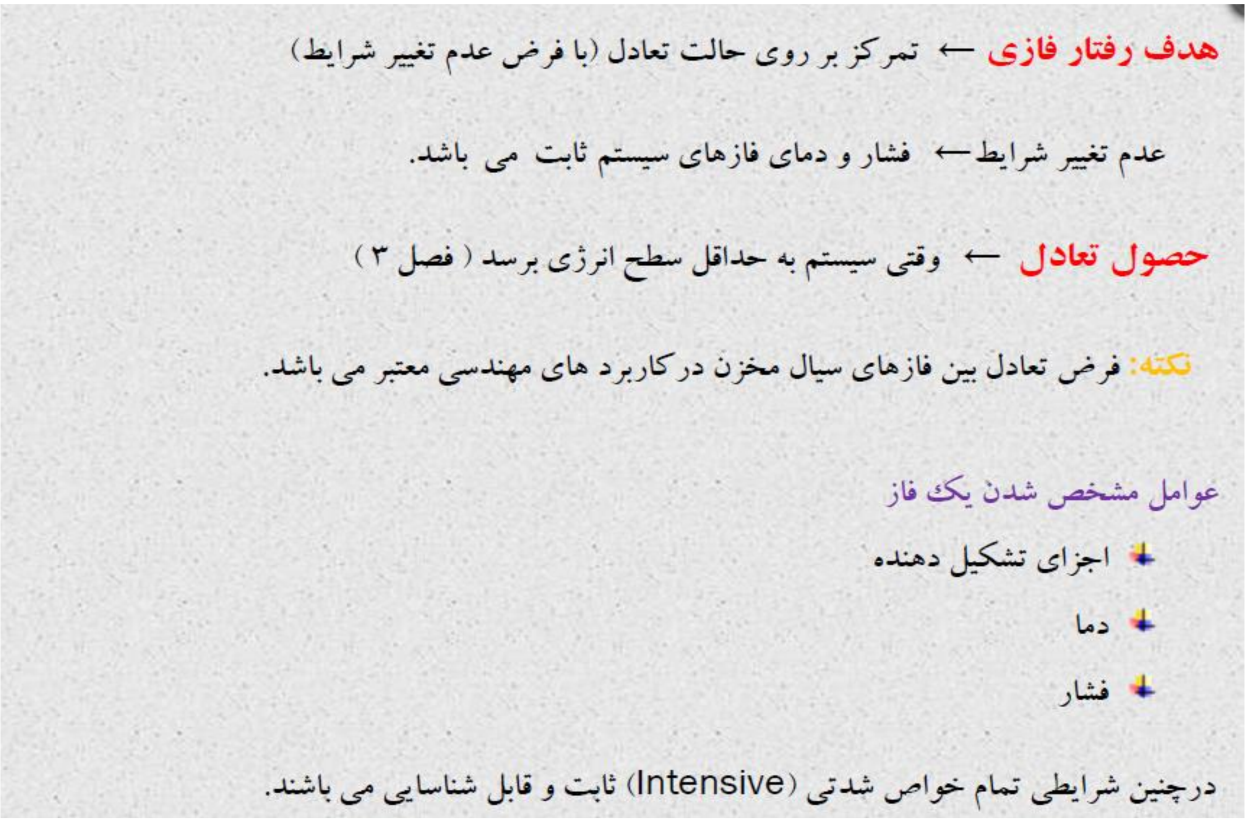
سیستم: جرمی از ماده که در محیطی مسدود شده باشد.

سیستم همگن: خواص متمرکز (Intensive) تغییر مستمر و یکنواخت ← تک فاز

سیستم غیر همگن: خواص متمرکز (Intensive) در حد فاصل فازها تغییر ناگهانی دارند ← چند فاز

Intensive: به مقدار جرم بستگی **ندارند** (T, P, z, v, ρ) ➡

Extensive: به مقدار جرم موجود (جرم کلی) بستگی **دارد** (جرم و حجم کلی)



هدف رفتار فازی ← تمرکز بر روی حالت تعادل (با فرض عدم تغییر شرایط)

عدم تغییر شرایط← فشار و دمای فازهای سیستم ثابت می باشد.

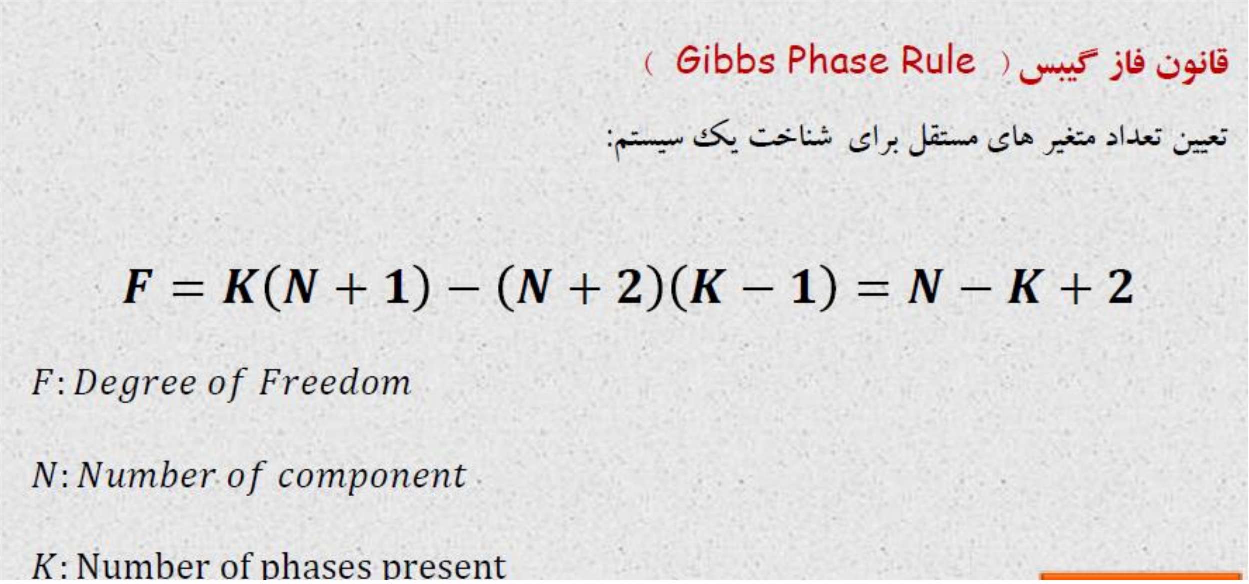
حصول تعادل ← وقتی سیستم به حداقل سطح انرژی برسد (فصل ۳)

نکته: فرض تعادل بین فازهای سیال مخزن درکاربرد های مهندسی معتبر می باشد.

عوامل مشخص شدن یک فاز

- اجزای تشکیل دهنده
- دما
- فشار

درچنین شرایطی تمام خواص شدتی (Intensive) ثابت و قابل شناسایی می باشند.



قانون فاز گیبس (Gibbs Phase Rule)

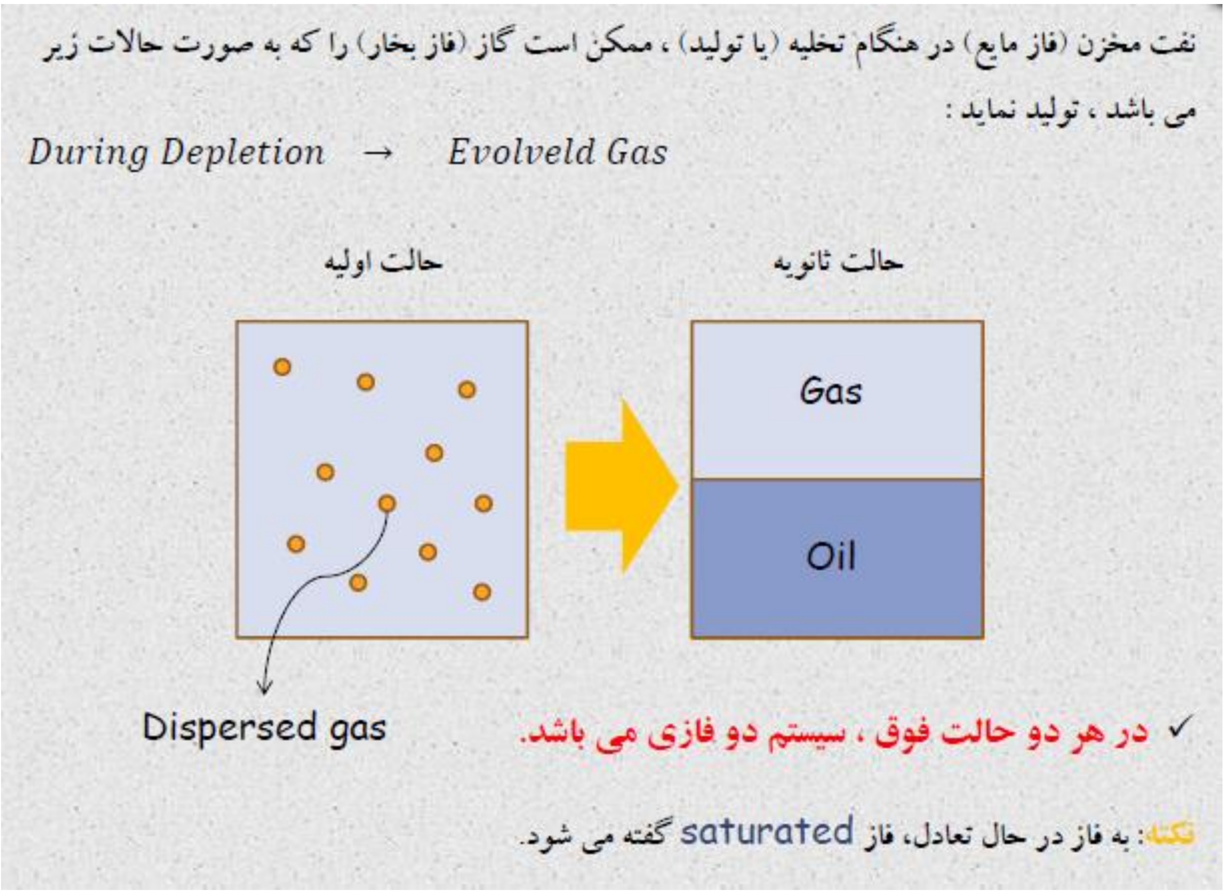
تعیین تعداد متغیر های مستقل برای شناخت یک سیستم:

$$F = K(N+1) - (N+2)(K-1) = N - K + 2$$

F: *Degree of Freedom*

N: *Number of component*

K: Number of phases present



نفت مخزن (فاز مایع) در هنگام تخلیه (یا تولید) ، ممکن است گاز (فاز بخار) را که به صورت حالات زیر می باشد ، تولید نماید :

During Depletion → *Evolveld Gas*

✓ در هر دو حالت فوق ، سیستم دو فازی می باشد.

نکته: به فاز در حال تعادل، فاز saturated گفته می شود.

Pure Component

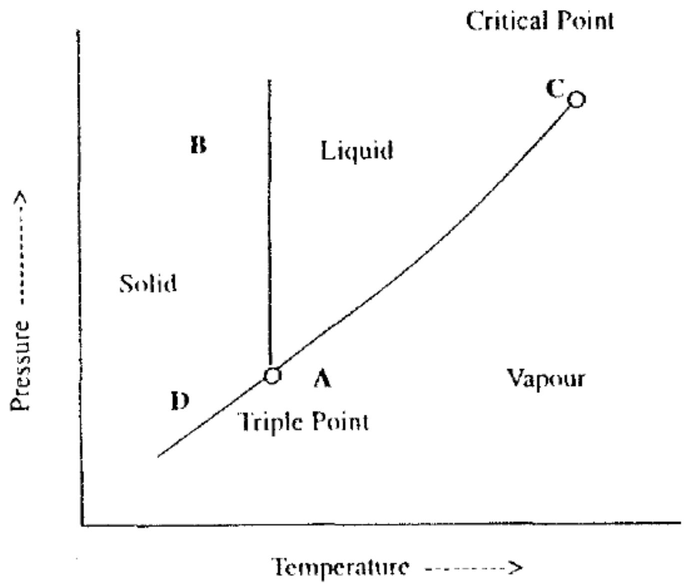
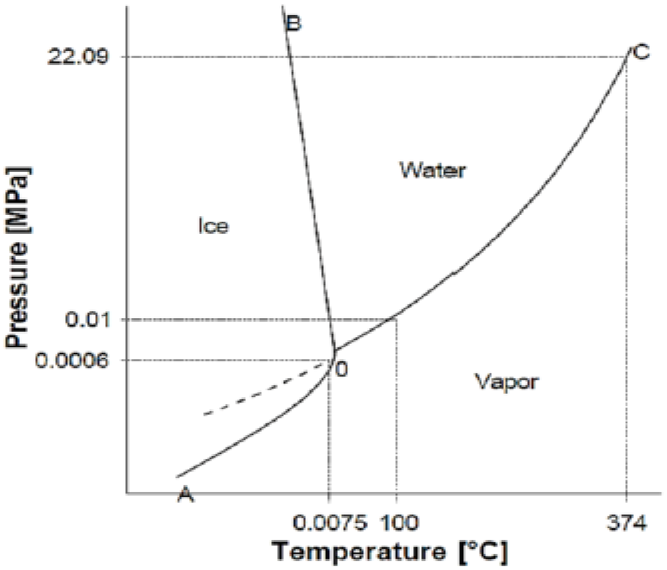
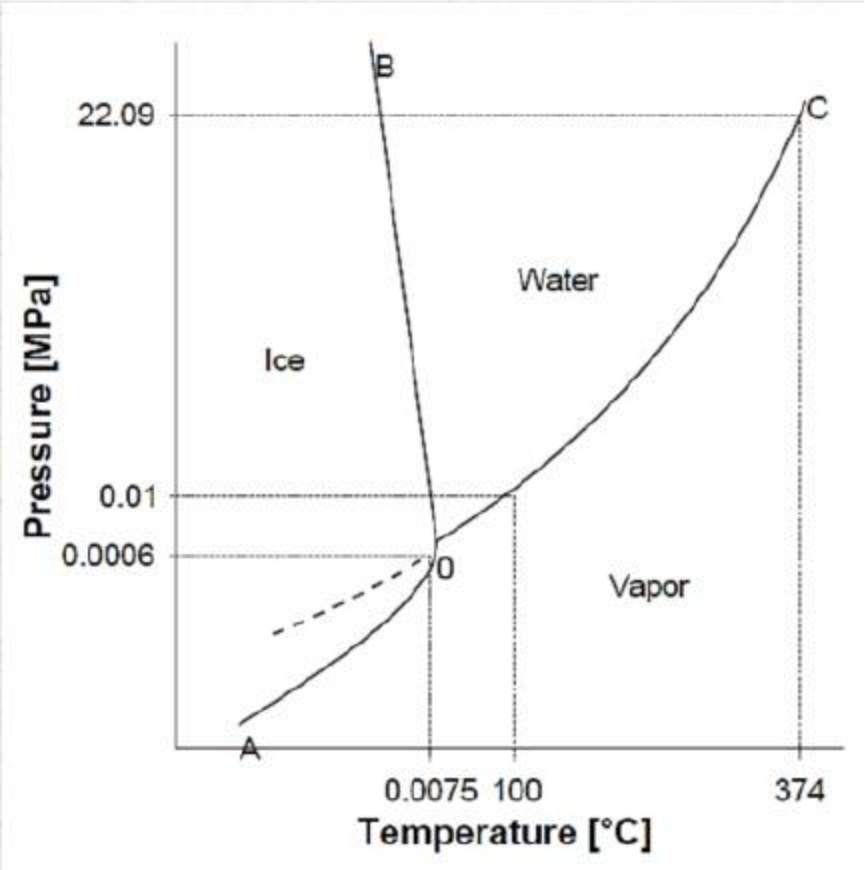
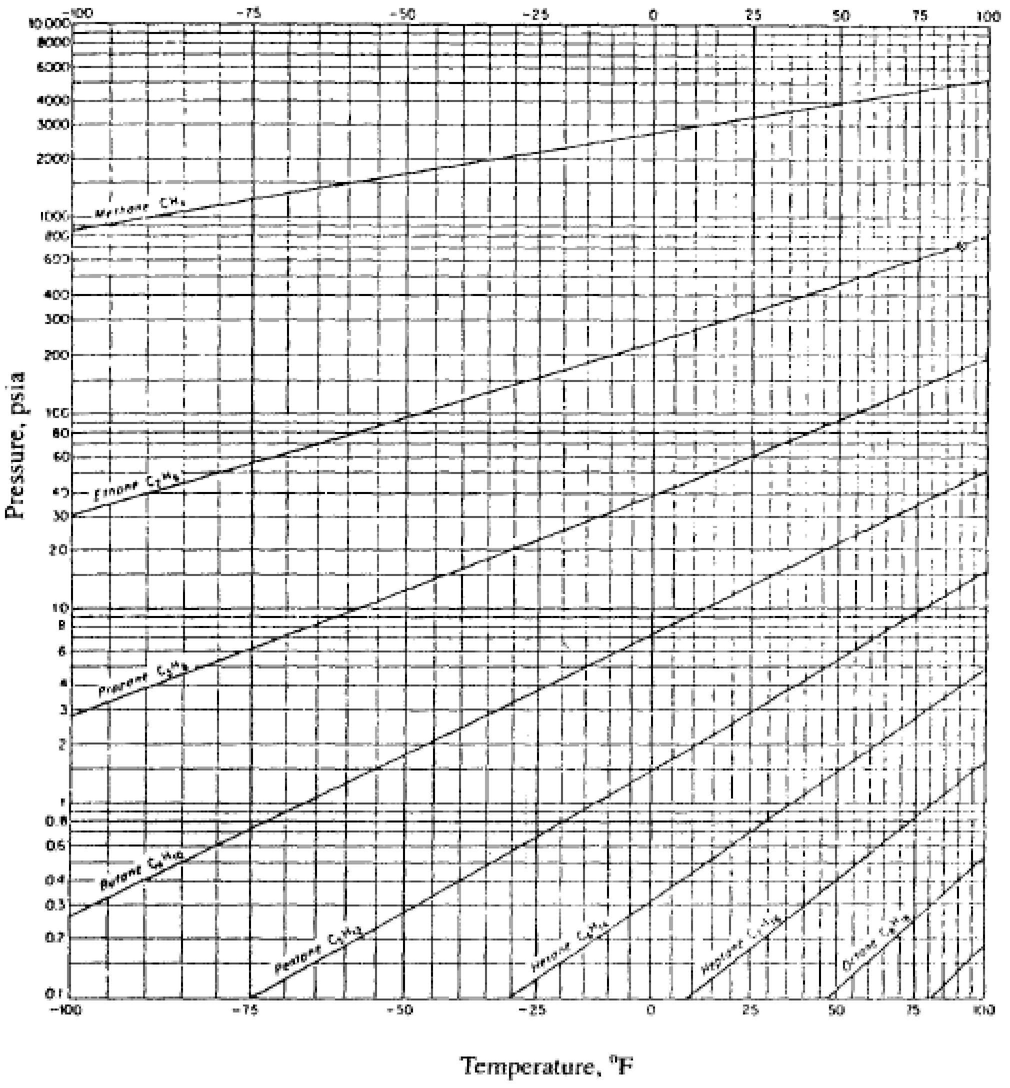


Figure 1.2. Pressure-temperature diagram of pure substance.



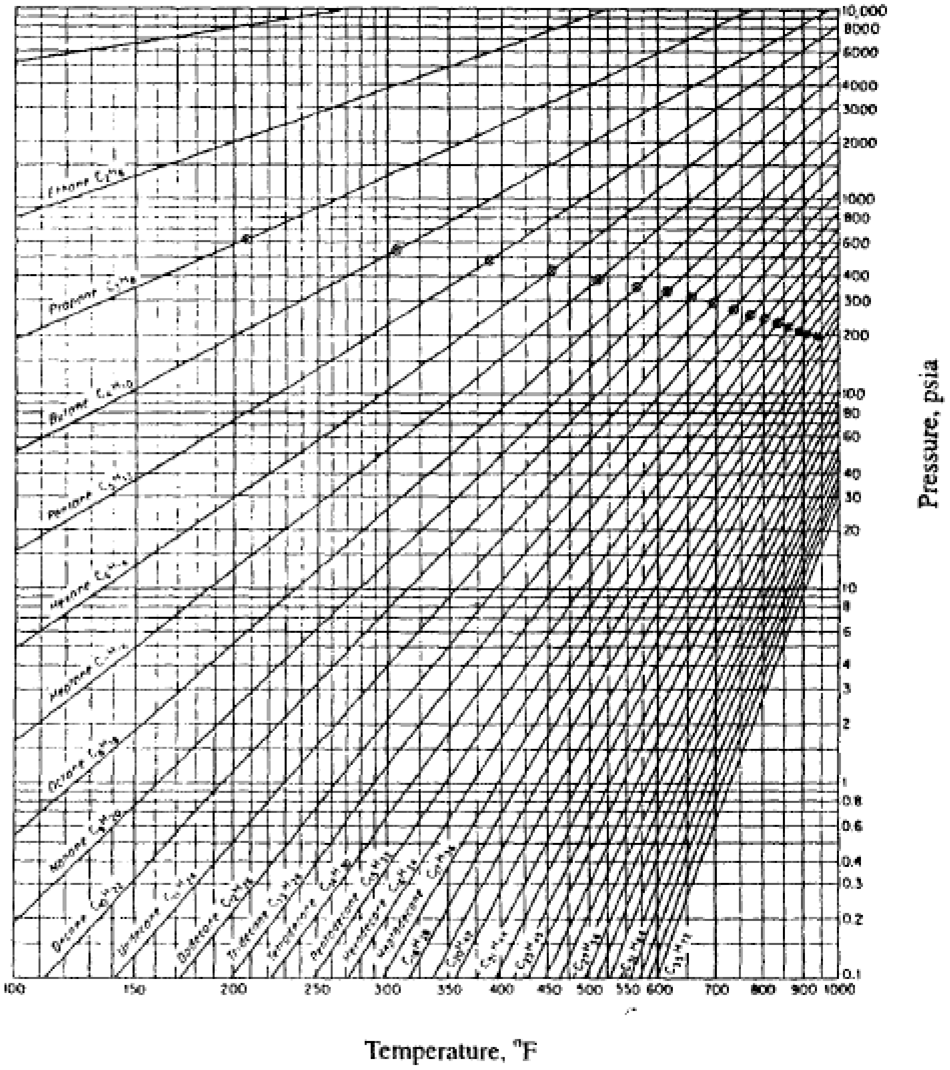
Water Phase diagram (Pure component)





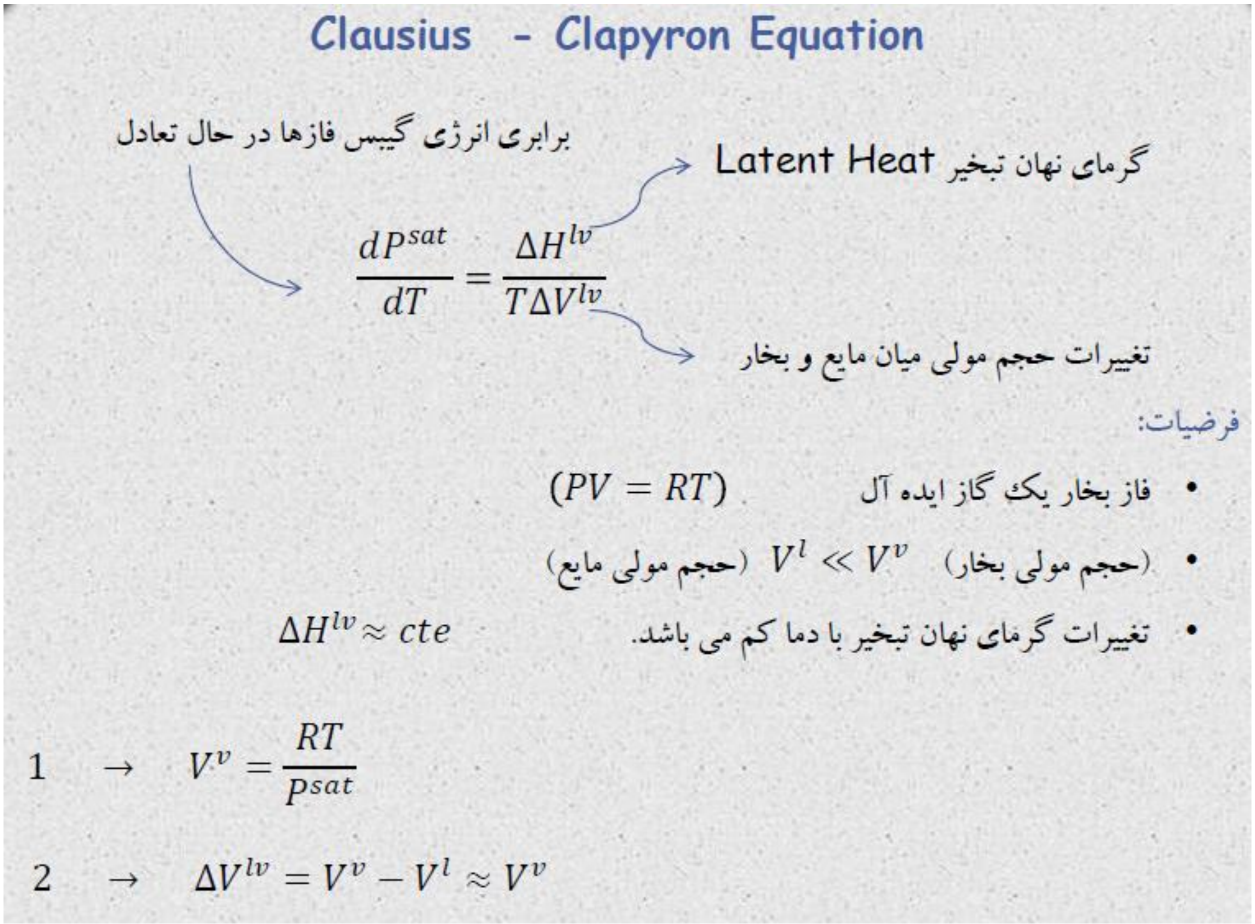
K=(°F+459.67)/1.8 MPa=0.006895 psia

Figure 1.3. Vapour pressure of normal paraffins. McGraw-Hill Companies Copyright. Reproduced from [8] with permission.



K=(°F+459.67)/1.8 MPa=0.006895 psia

Figure 1.3 (Cont). Vapour pressure of normal paraffins. McGraw-Hill Companies Copyright. Reproduced from [8] with permission.



Clausius - Clapyron Equation

برابری انرژی گیبس فازها در حال تعادل

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\Delta V^{lv}}$$

گرمای نهان تبخیر Latent Heat

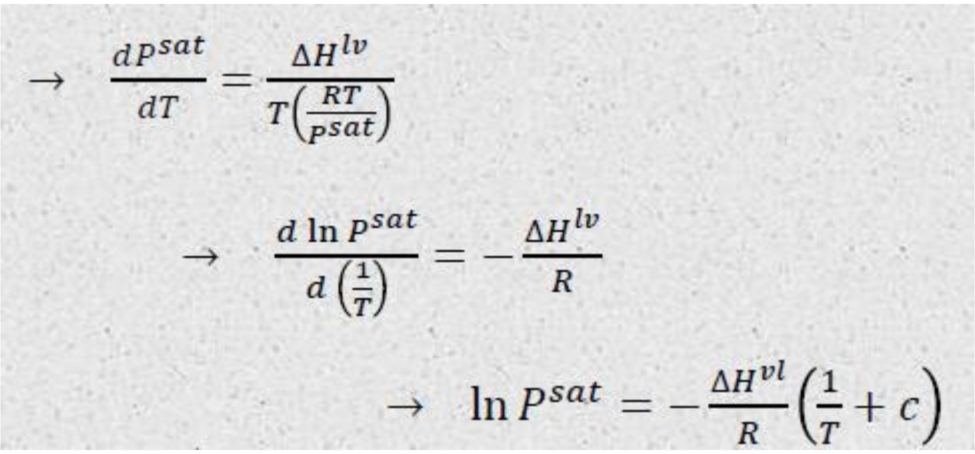
تغییرات حجم مولی میان مایع و بخار

فرضیات:

- فاز بخار یک گاز ایده آل $(PV = RT)$
- (حجم مولی بخار) $V^l \ll V^v$ (حجم مولی مایع)
- تغییرات گرمای نهان تبخیر با دما کم می باشد. $\Delta H^{lv} \approx cte$

$$1 \quad \rightarrow \quad V^v = \frac{RT}{P^{sat}}$$

$$2 \quad \rightarrow \quad \Delta V^{lv} = V^v - V^l \approx V^v$$



$$\rightarrow \quad \frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\left(\frac{RT}{P^{sat}}\right)}$$

$$\rightarrow \quad \frac{d\ln P^{sat}}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^{lv}}{R}$$

$$\rightarrow \quad \ln P^{sat} = -\frac{\Delta H^{vl}}{R}\left(\frac{1}{T} + c\right)$$

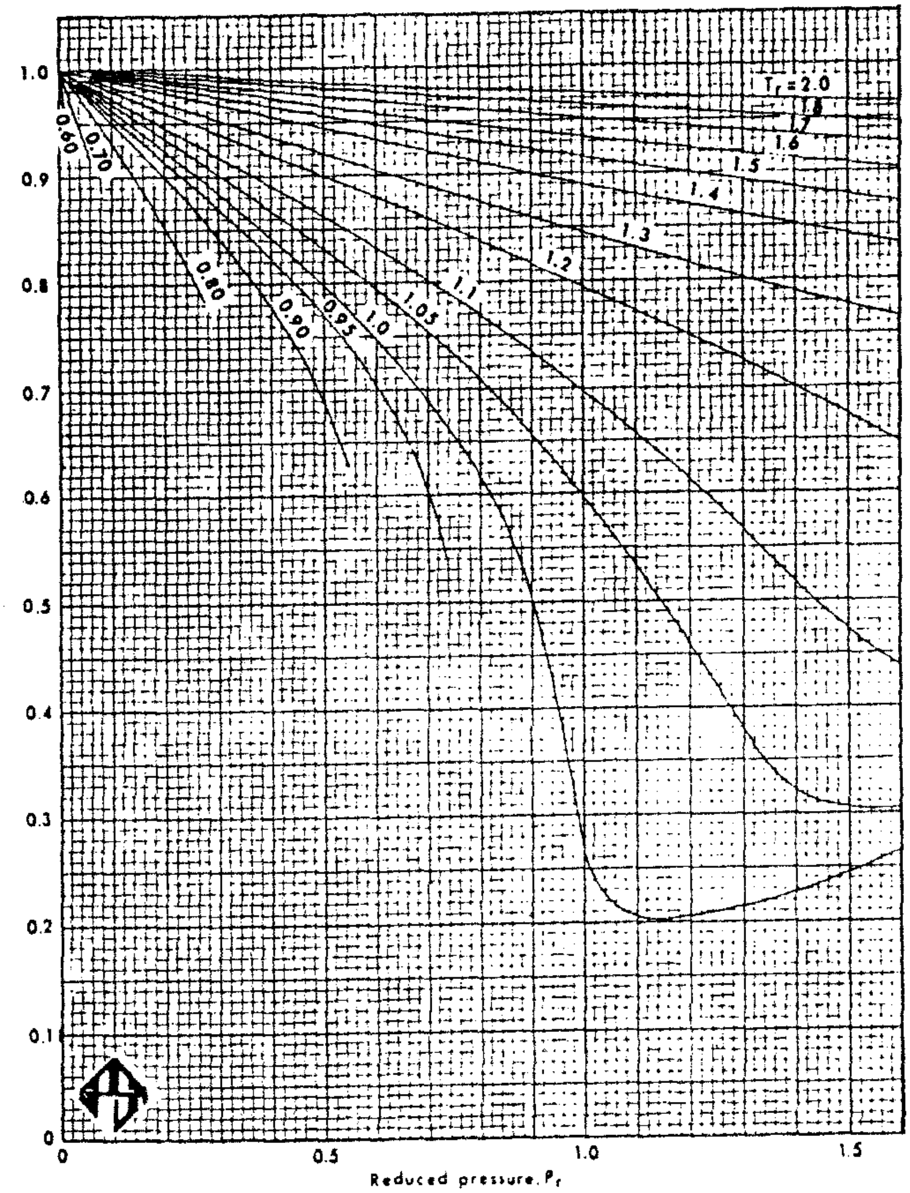
Antoine: $$\ln P^{sat} = A - \frac{B}{T + C}$$

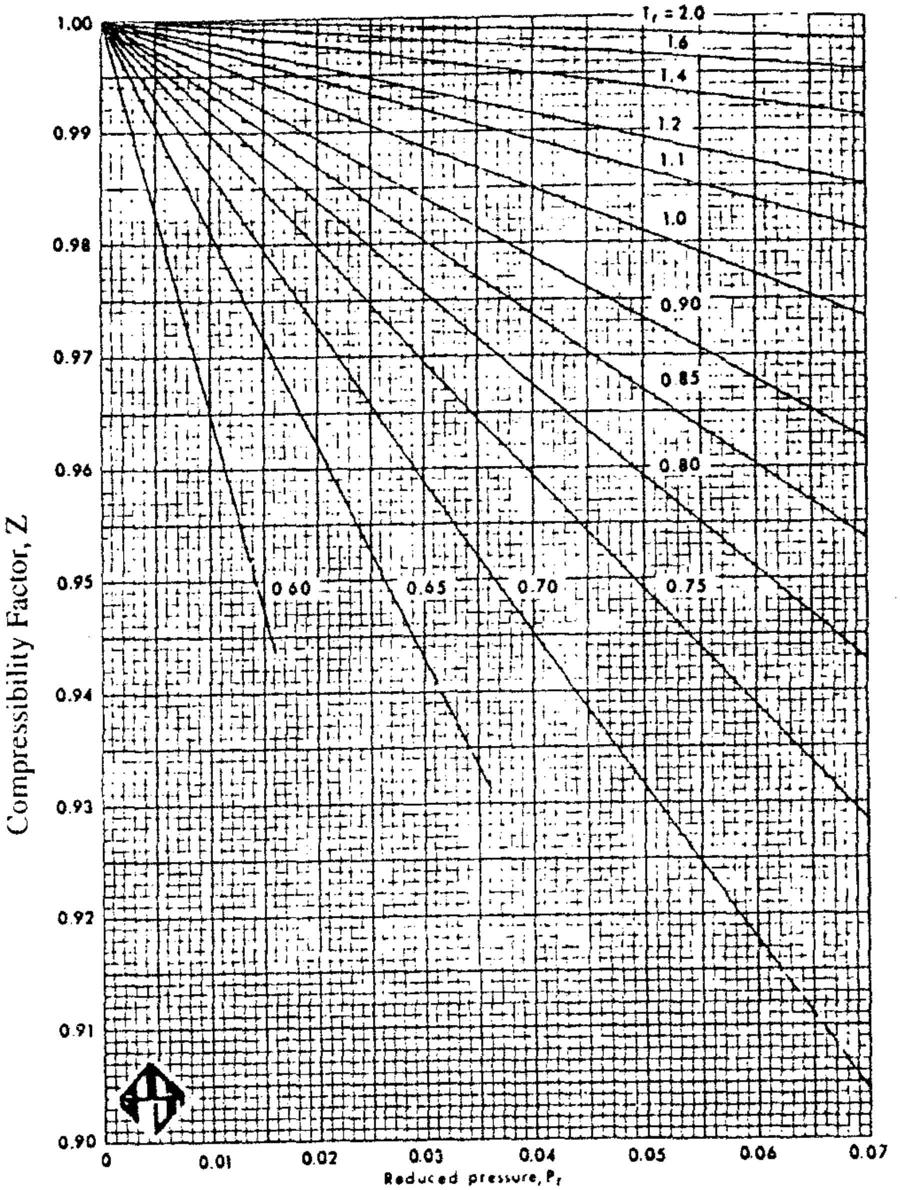
Corresponding Theory

$Z=PV/(RT)$ Compressibility factor

$T_r=T/T_c$

$P_r=P/P_c$


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1.0
1.5
Reduced pressure, P_r
T_r = 2.0
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.05
1.0
0.95
0.90
0.80
0.70
0.60



Compressibility factor Chart

$$\omega = -\log(P^s / P_c)_{(\text{at } T_r = 0.7)} - 1.0 \tag{1.9}$$

Lee-Kesler correlation

phase equilibria. For example, the vapour pressure of pure compounds can be reliably estimated using the Lee and Kesler [12] correlation which is based on the three parameter corresponding states,

$$P^s / P_c = \exp(f^{(0)} + \omega f^{(1)}) \tag{1.10}$$

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

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

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

Example 1.1.

Calculate the vapour pressure of normal hexane at 355.15 K, using:
(a) the Cox chart, (b) the Lee-Kesler equation.

Solution:

(a) From Figure 1.3, at T=355.15 K (179.6 °F), the vapour pressure is read equal to 0.15 MPa (21 psia).

(b) The critical properties of normal hexane are read from Table A.1 in Appendix A, and used in Eq.(1.10) to calculate the vapour 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 generalised correlations to predict volumetric data has also proved successful. An example is the Rackett equation [13] for the saturated molar volume of pure compounds,

$$v^s / v_c = Z_c^{(1-T_r)^{2/7}} \tag{1.11}$$

where v^s, and v_c are the saturated liquid and critical molar volumes, respectively. A more reliable estimation of the liquid molar volume is expected from the modification of the Rackett equation by Spencer and Danner [14], where the critical compressibility factor has been replaced by the parameter Z_{RA}, known as the Rackett compressibility factor,

$$v^s = (RT_c / P_c) Z_{RA}^{[1+(1-T_r)^{2/7}]} \tag{1.12}$$

The values of Z_{RA} for some substances [15] are given in Table A.1 in Appendix A. For other compounds, it can be estimated from the Yamada-Gunn correlation [16]:

$$Z_{RA} = 0.29056 - 0.08775\omega \tag{1.13}$$

The application of acentric factor and critical compressibility factor in developing generalised correlations will be described further, particularly in Chapter 4 dealing with equations of state.

Example 1.2.

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 Table A.1 in Appendix A and substituting them in Eq.(1.12), 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:
$V=m/\rho=1/425.3=0.002351\ m^3$

The cylinder pressure remains constant, equal to the normal butane vapour pressure, as long as the mixture remains two phases at 393 K. The vapour pressure can be calculated from the Lee-Kesler equation, Eq.(1.10), similar to that in Example 1.1, which results in:

$P^s=2.2160$ MPa, at 393 K.

The vapour density at the above conditions can be calculated from Eq.(1.7). The compressibility factor, Z, is read from Figure 1.8, at prevailing reduced values of: $P_r=P/P_c= 2.216/3.796=0.5838$ and $T_r=0.9244$, to be $Z=0.67$. The universal gas constant is read, from Table A.3 in Appendix A, to be 0.0083144 $MPa.m^3/(K.kgmol)$.

Hence,

$v = ZRT / P = 1.003\ m^3/kgmol$, and the vapour density is ,

$\rho^V=M/v^V=58.123/1.003=57.95\ kg/m^3$

The mass balance results in,

$m=V^L \rho^L+ V^V \rho^V$

$0.5=V^L\times425.3 +(0.002351-V^L)\times 57.95$

Liquid butane volume, $V^L=0.0009902\ m^3$

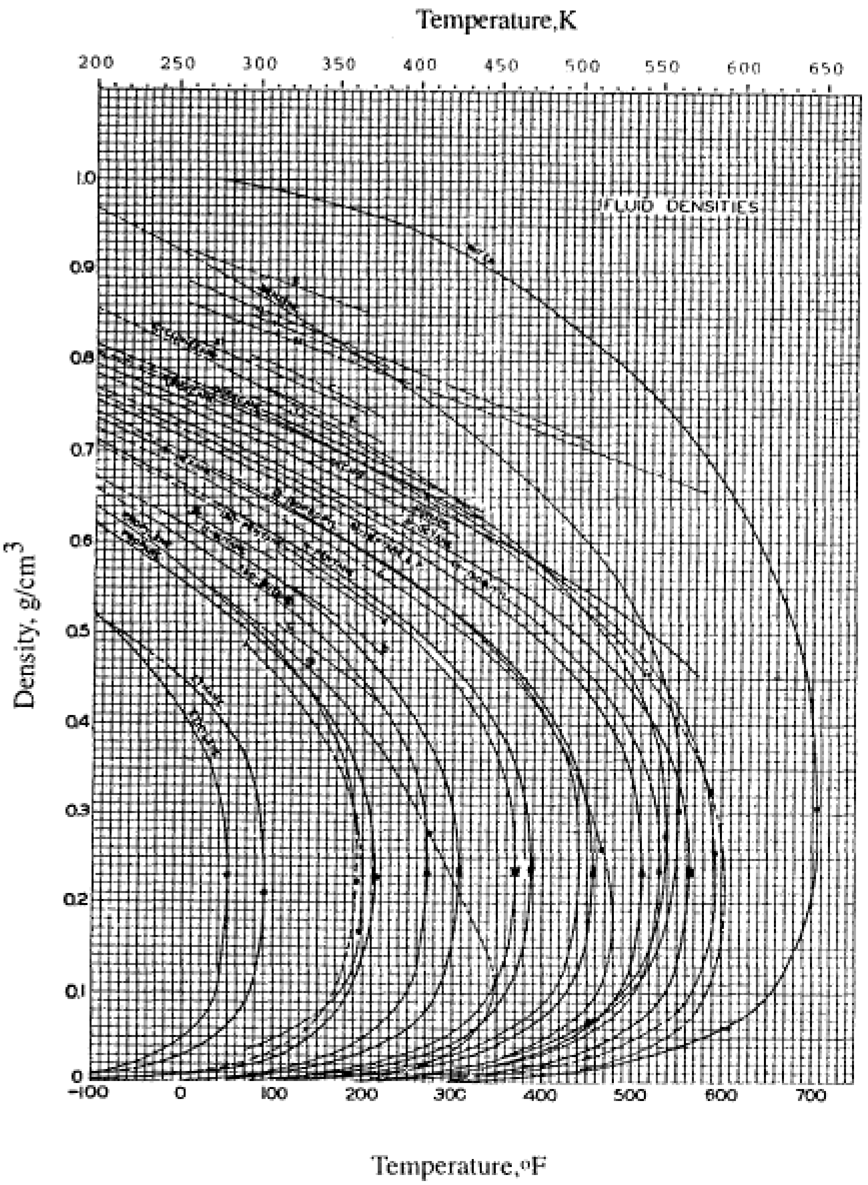


Figure 1.4. Saturated fluid density of pure compounds (curves identified by letters are related to binary and multicomponent fluids described in Reference 8). McGraw-Hill Companies Copyright. Reproduced from [8] with permission.

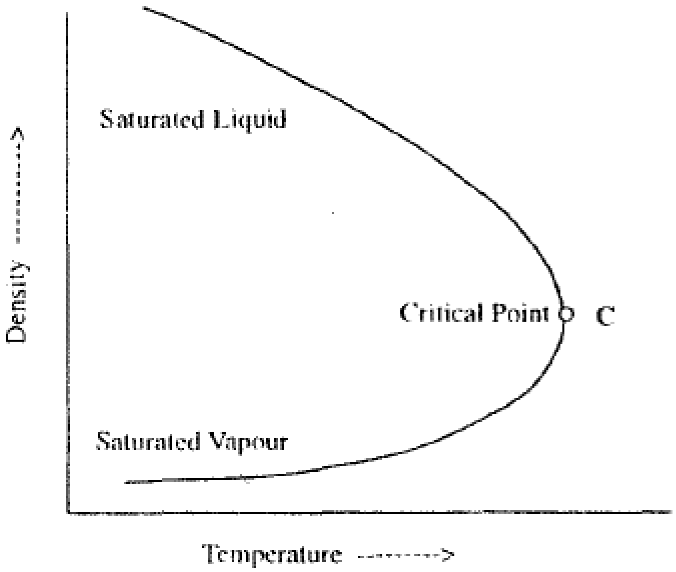


Figure 1.5. Variations of saturated fluid density with temperature.

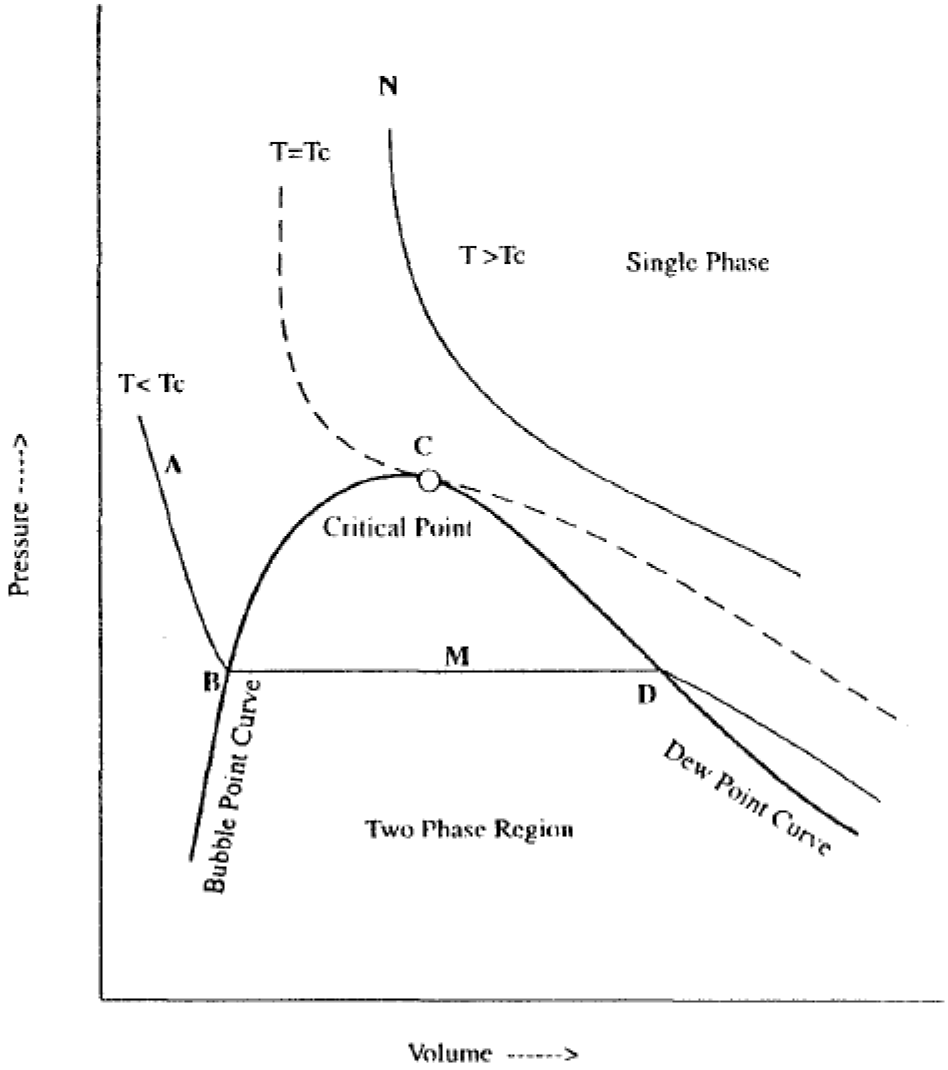


Figure 1.7. Pressure-volume diagram of pure fluid.

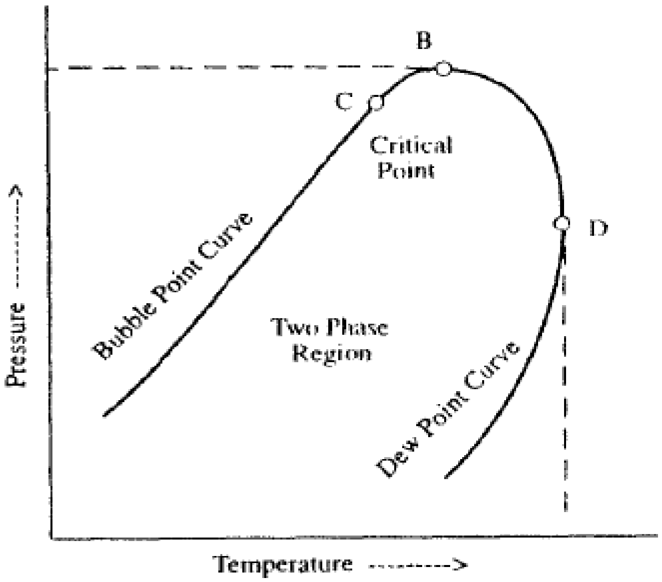


Figure 1.9. Schematic pressure-temperature diagram of a binary mixture.

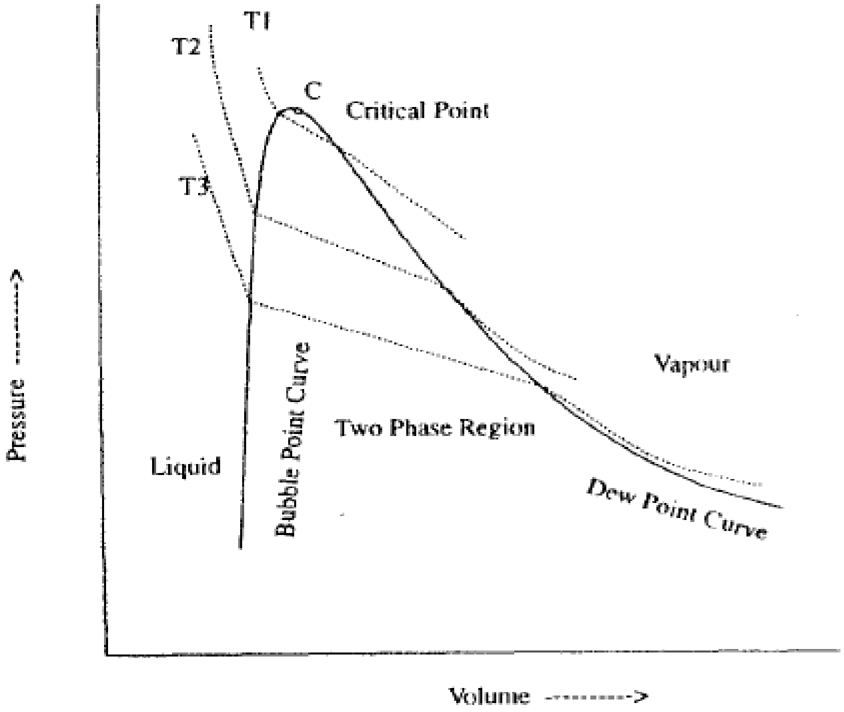


Figure 1.10. Pressure-volume diagram of binary mixtures.

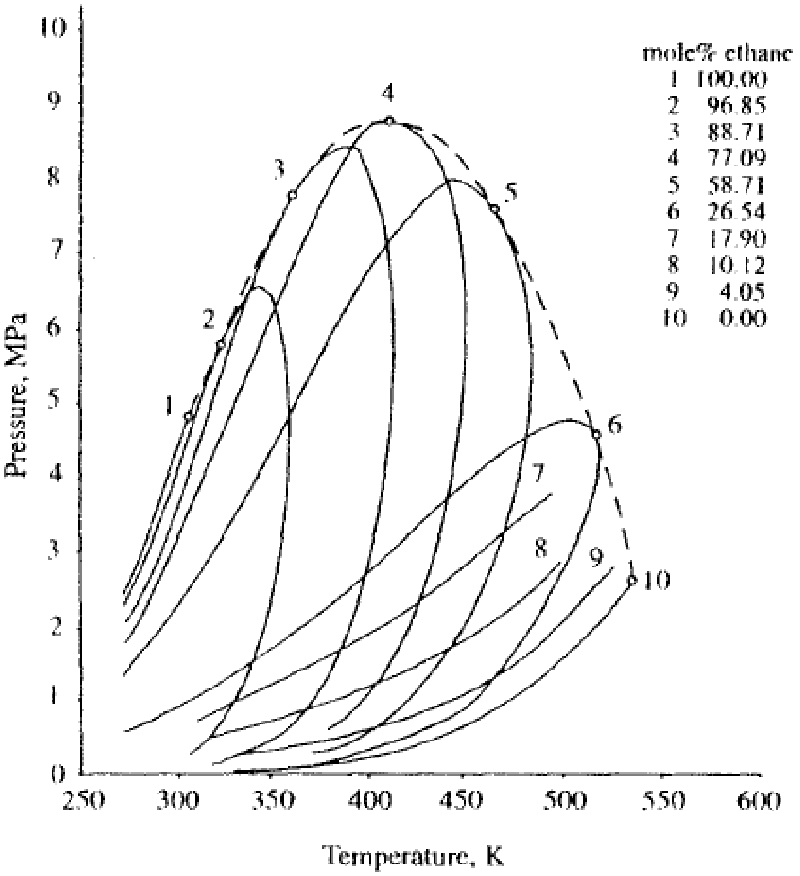


Figure 1.11. Phase diagram of ethane - normal heptane. McGraw-Hill Companies Copyright. Reproduced from [8] with permission.

Figure 1.13. Vapour 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.

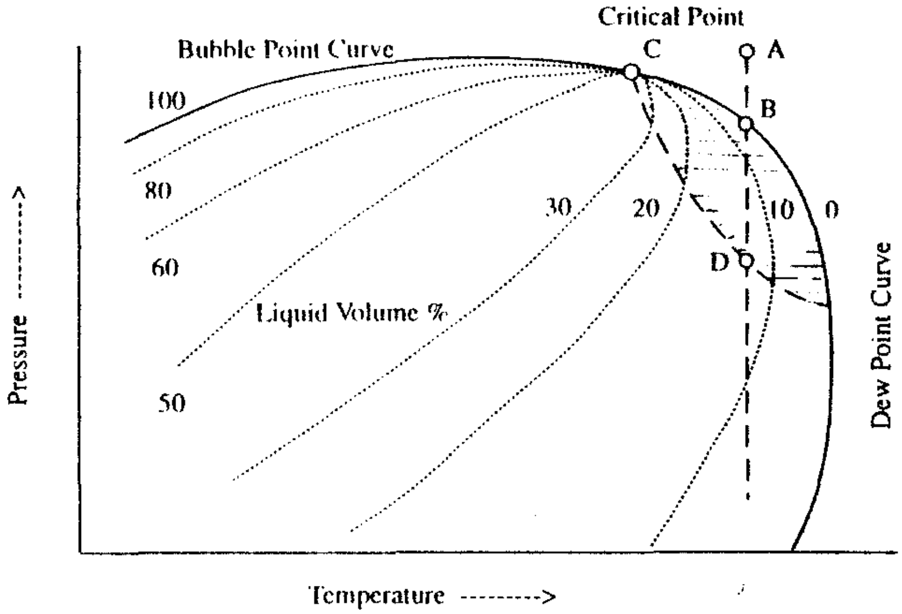


Figure 1.13. Phase diagram of a multicomponent mixture.

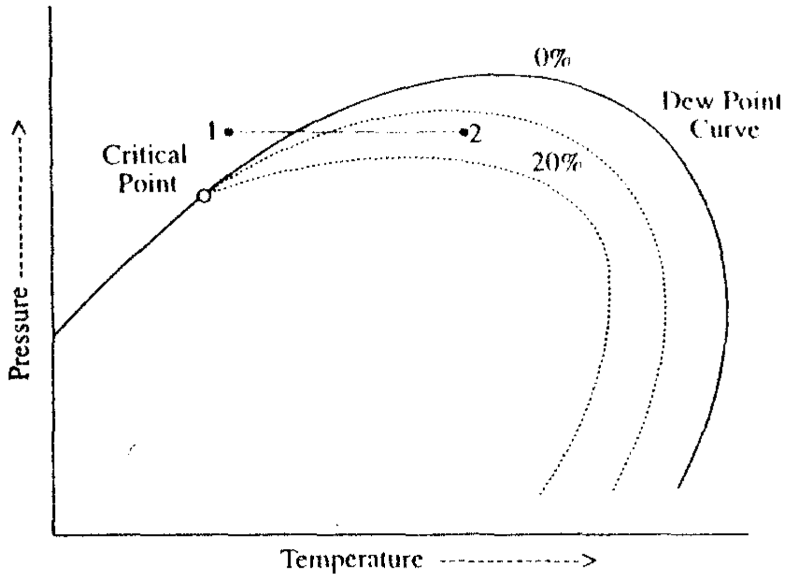


Figure 1.14. Retrograde condensation at constant pressure.

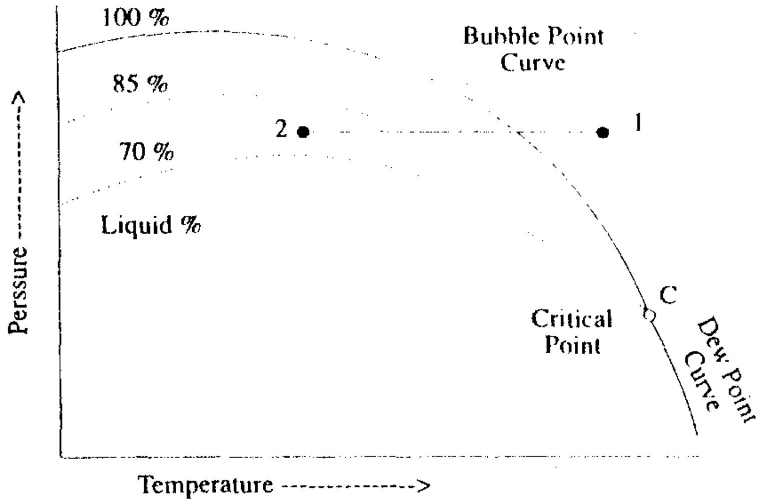


Figure 1.15. Retrograde vaporisation at constant pressure.

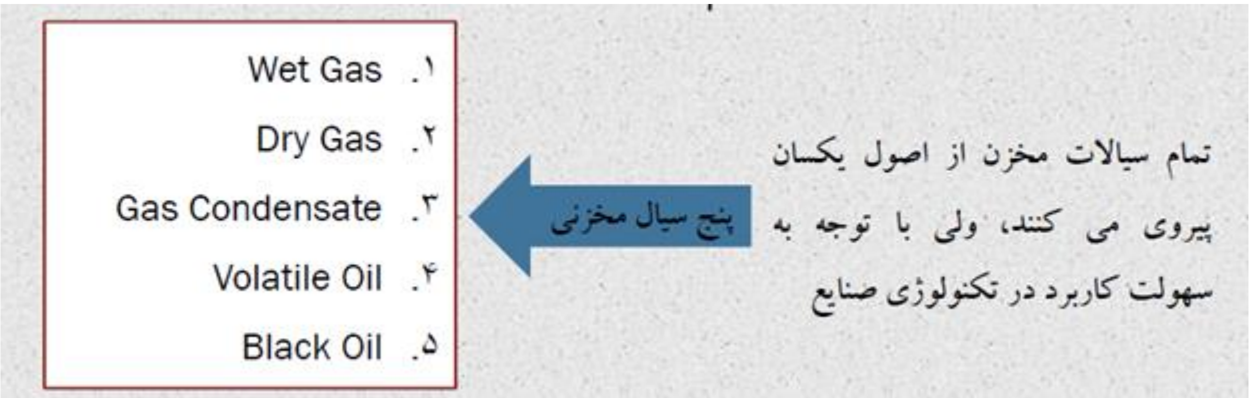
1.3 CLASSIFICATION OF RESERVOIR FLUIDS

The typical phase diagram of a reservoir hydrocarbon system, shown in Figure 1.13, 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 vaporise 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 behaviour of a reservoir fluid is determined by its composition. Typical compositions of various classes of reservoir hydrocarbon fluids are given in Table 1.2. 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.

Table 1.2.
Typical compositions of various reservoir fluids.

Component, Mole%	Dry Gas	Gas Condensate	Volatile Oil	Black Oil
N2	6.25	0.29	0.12	0.16
CO2	2.34	1.72	1.50	0.91
C1	81.13	79.14	69.59	36.47
C2	7.24	7.48	5.31	9.67
C3	2.35	3.29	4.22	6.95
iC4	0.22	0.51	0.85	1.44
nC4	0.35	1.25	1.76	3.93
iC5	0.09	0.36	0.67	1.44
nC5	0.03	0.55	1.12	1.41
C6		0.61	1.22	4.33
C7+		4.80	16.64	33.29



تمام سیالات مخزن از اصول یکسان پیروی می کنند، ولی با توجه به سهولت کاربرد در تکنولوژی صنایع

پنج سیال مخزنی

۱. Wet Gas
۲. Dry Gas
۳. Gas Condensate
۴. Volatile Oil
۵. Black Oil

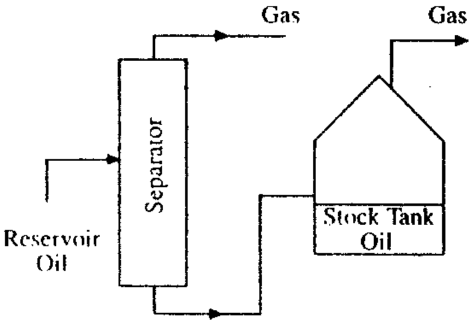


Figure 1.19. Schematic diagram of stabilising produced oil as stock tank oil and gas at standard conditions.

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,

$$^{o}API = (141.5/S_o) - 131.5 \qquad (1.17)$$

where S_o is the stock tank oil specific gravity, or relative density, to water at 60 °F (288 K).

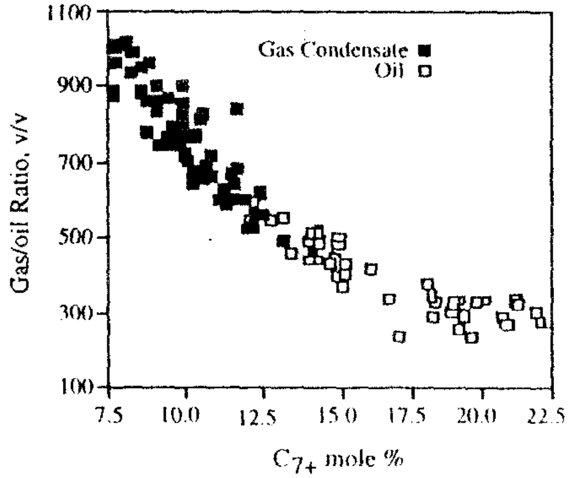


Figure 1.20. C_{7+}- GOR relation for typical oil and gas condensate fluids. Courtesy of Hart Publication Inc. Reproduced from [19].

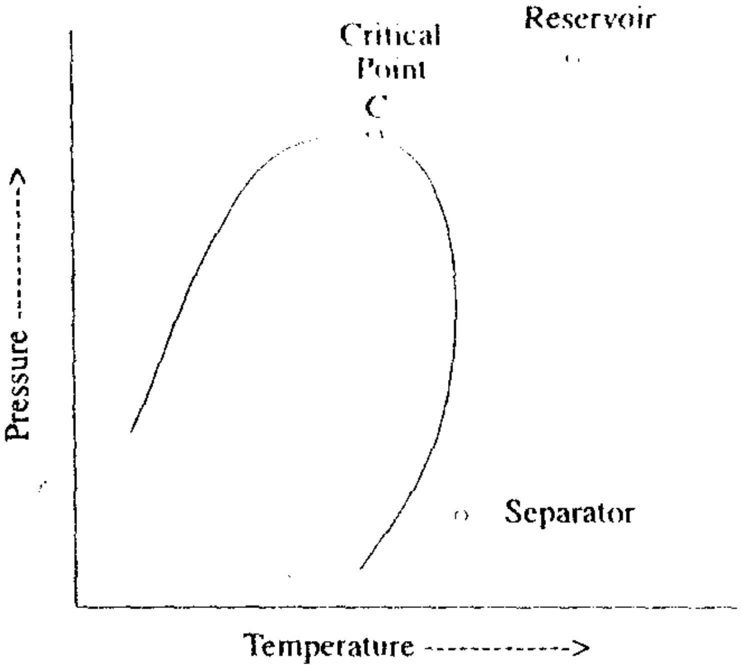


Figure 1.21. Phase diagram of dry gas.

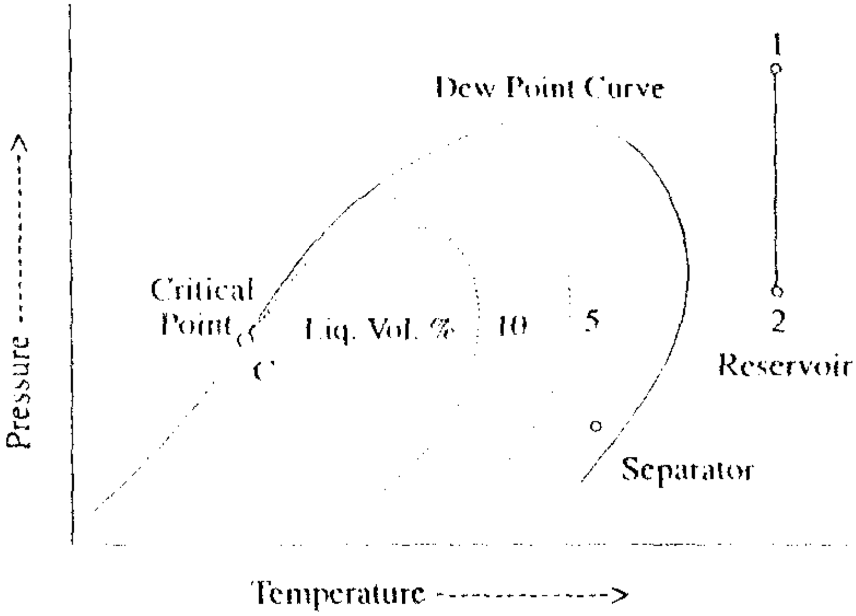


Figure 1.22. Phase diagram of wet gas.

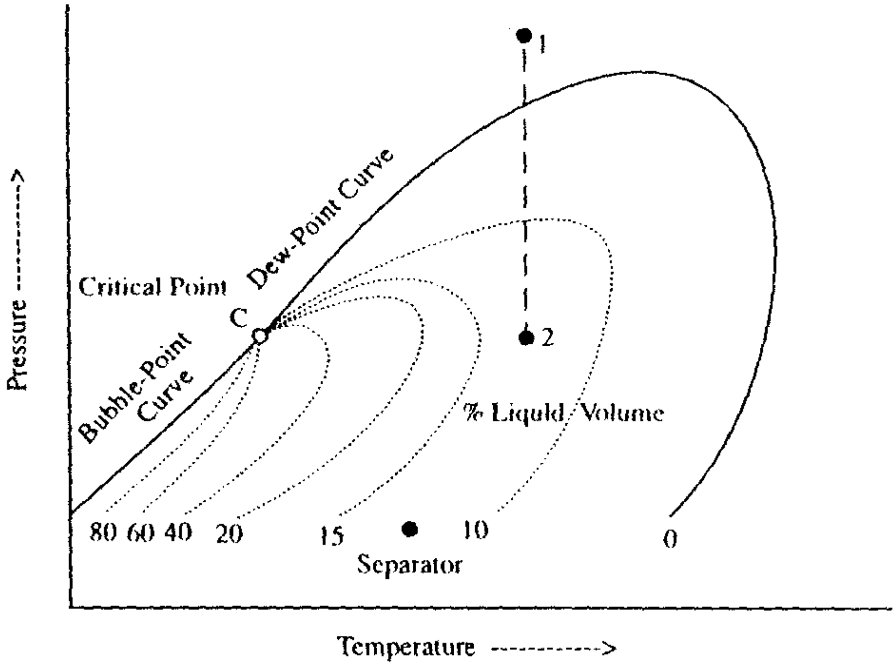


Figure 1.23. Phase diagram of gas condensate.

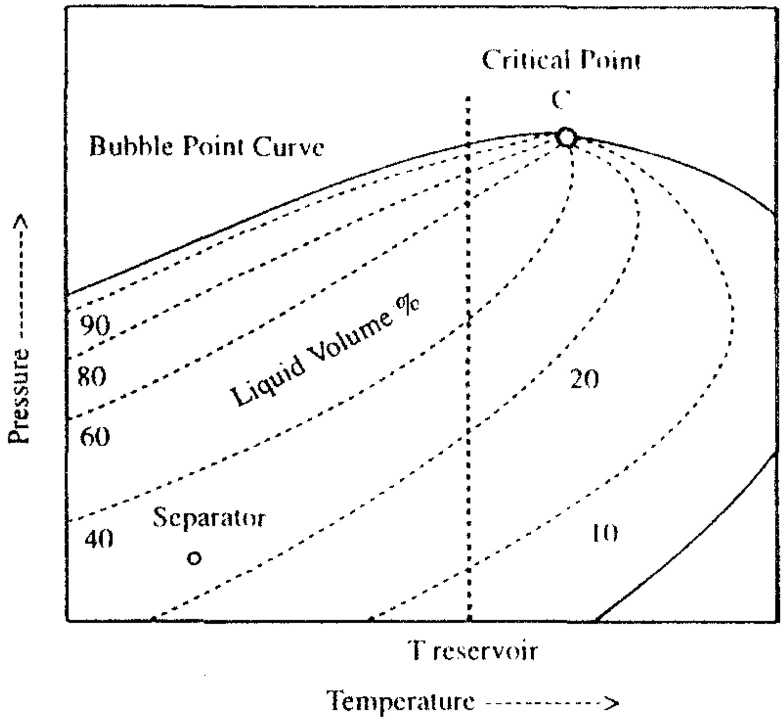


Figure 1.25. Phase diagram of a volatile oil.

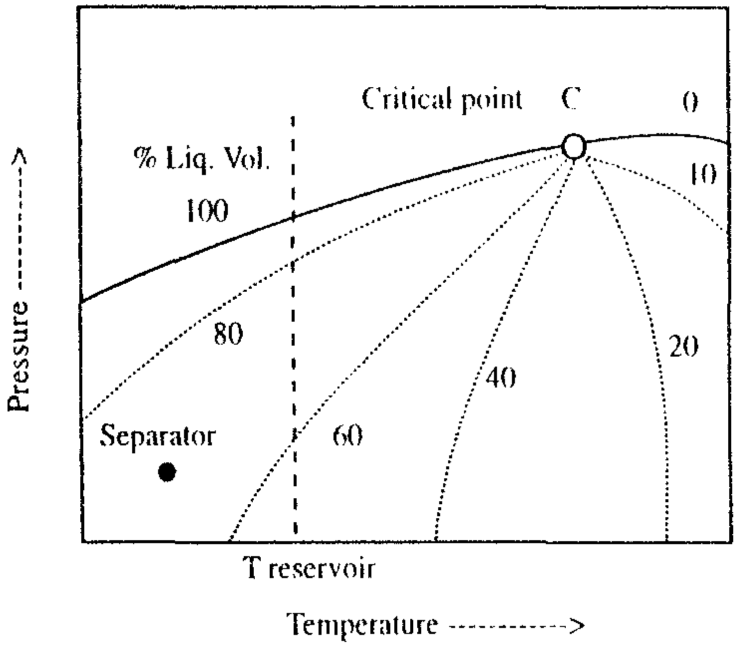
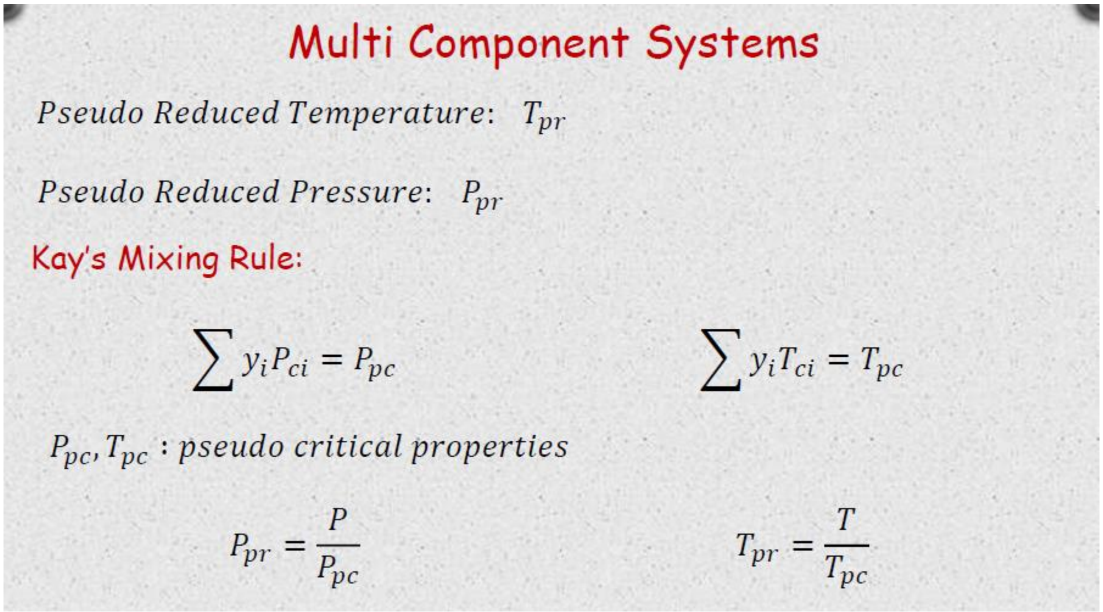


Figure 1.26. Phase diagram of a black oil.



Multi Component Systems

Pseudo Reduced Temperature: T_{pr}

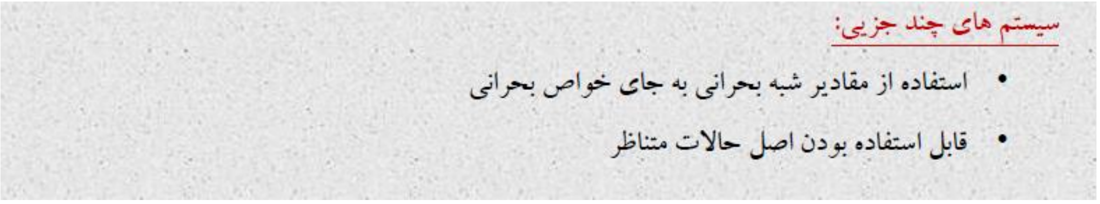
Pseudo Reduced Pressure: P_{pr}

Kay's Mixing Rule:

$$\sum y_i P_{ci} = P_{pc} \qquad \sum y_i T_{ci} = T_{pc}$$

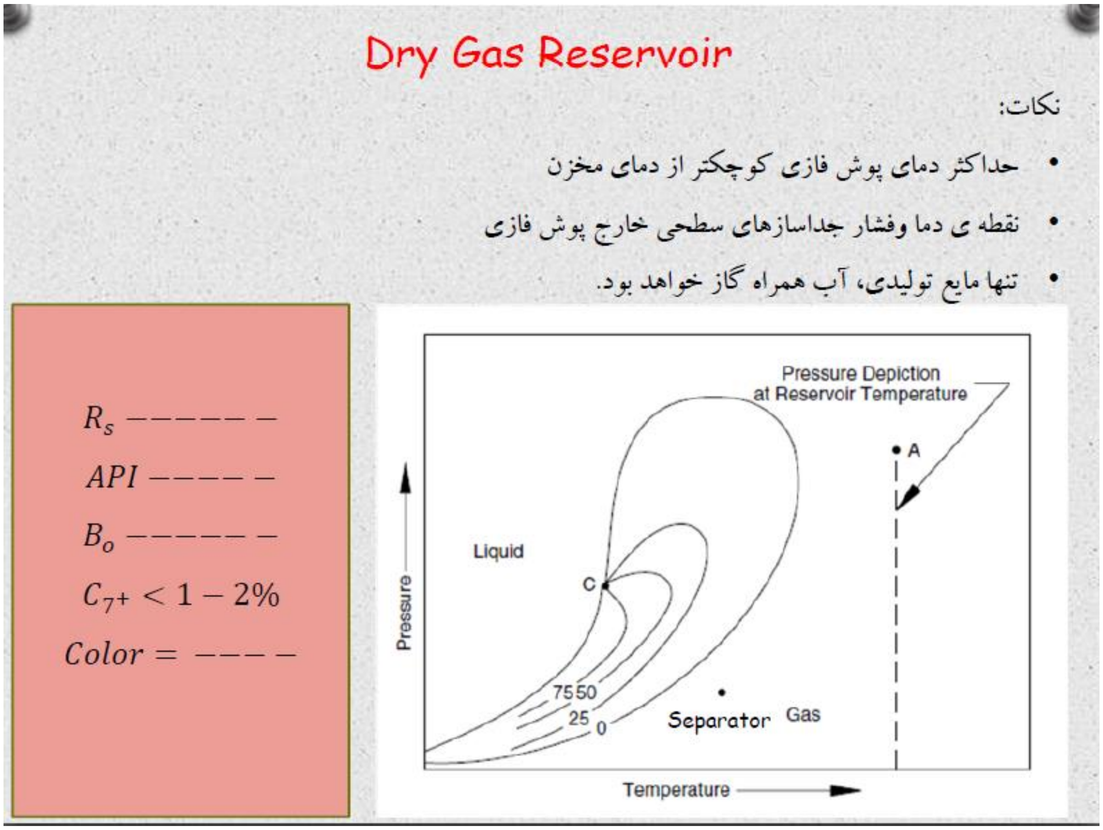
P_{pc}, T_{pc} : pseudo critical properties

$$P_{pr} = \frac{P}{P_{pc}} \qquad T_{pr} = \frac{T}{T_{pc}}$$



سیستم های چند جزیی:

- استفاده از مقادیر شبه بحرانی به جای خواص بحرانی
- قابل استفاده بودن اصل حالات متناظر



Dry Gas Reservoir

نکات:

- حداکثر دمای پوش فازی کوچکتر از دمای مخزن
- نقطه ی دما وفشار جداسازهای سطحی خارج پوش فازی
- تنها مایع تولیدی، آب همراه گاز خواهد بود.

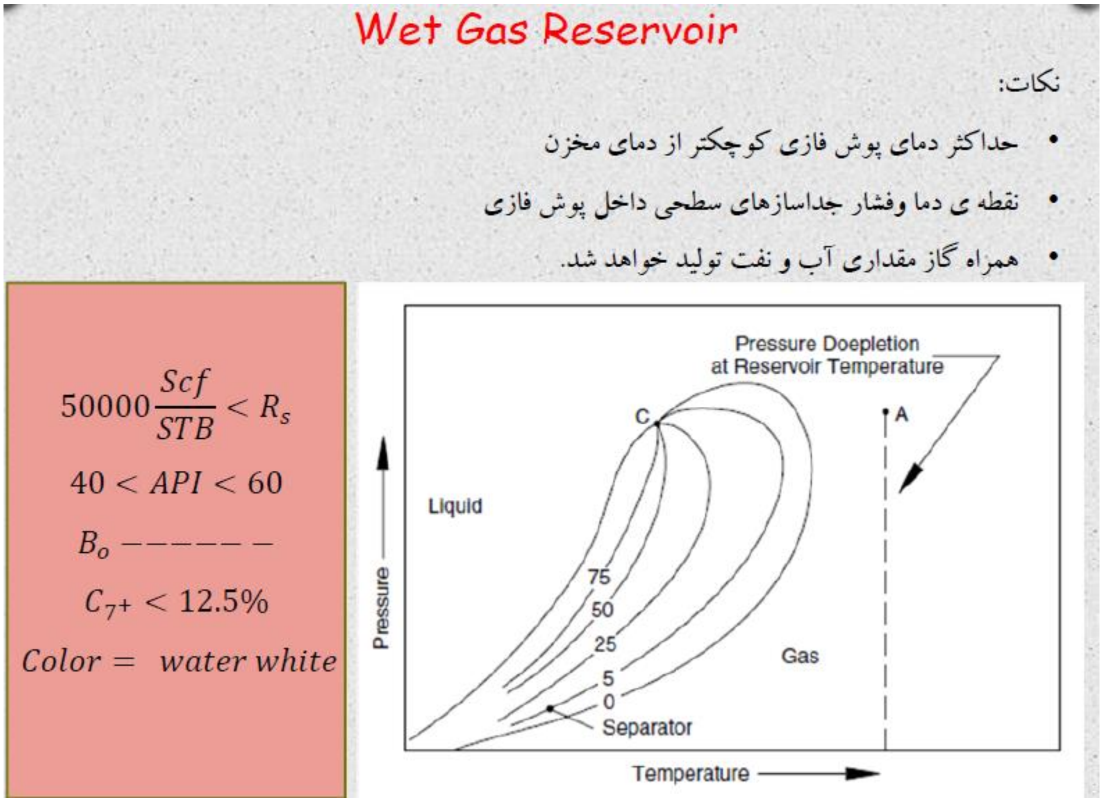
R_s ------ –

API ----- –

B_o ------ –

$C_{7+} < 1 - 2\%$

$Color =$ ---- –



Wet Gas Reservoir

نکات:

- حداکثر دمای پوش فازی کوچکتر از دمای مخزن
- نقطه ی دما وفشار جداسازهای سطحی داخل پوش فازی
- همراه گاز مقداری آب و نفت تولید خواهد شد.

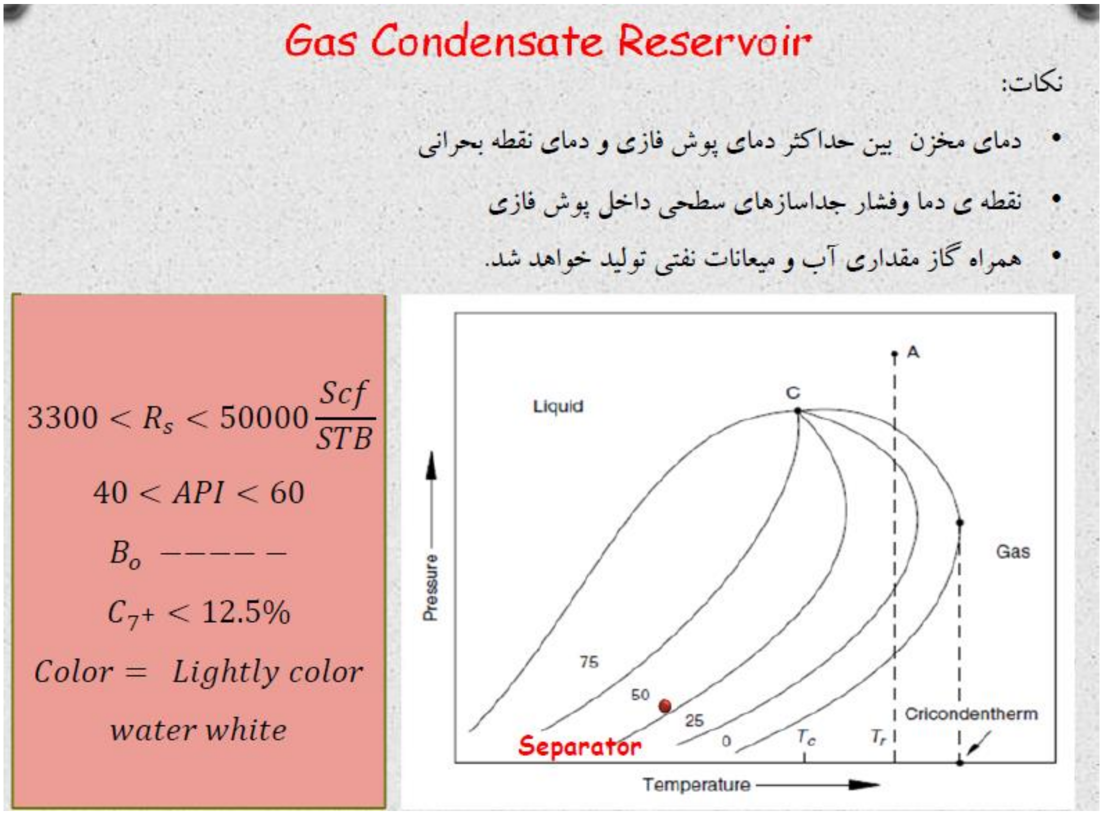
$$50000\frac{Scf}{STB} < R_s$$

$$40 < API < 60$$

$$B_o ------ -$$

$$C_{7+} < 12.5\%$$

$$Color = \ \ water\ white$$



Gas Condensate Reservoir

نکات:

- دمای مخزن بین حداکثر دمای پوش فازی و دمای نقطه بحرانی
- نقطه ی دما وفشار جداسازهای سطحی داخل پوش فازی
- همراه گاز مقداری آب و میعانات نفتی تولید خواهد شد.

$$3300 < R_s < 50000 \frac{Scf}{STB}$$

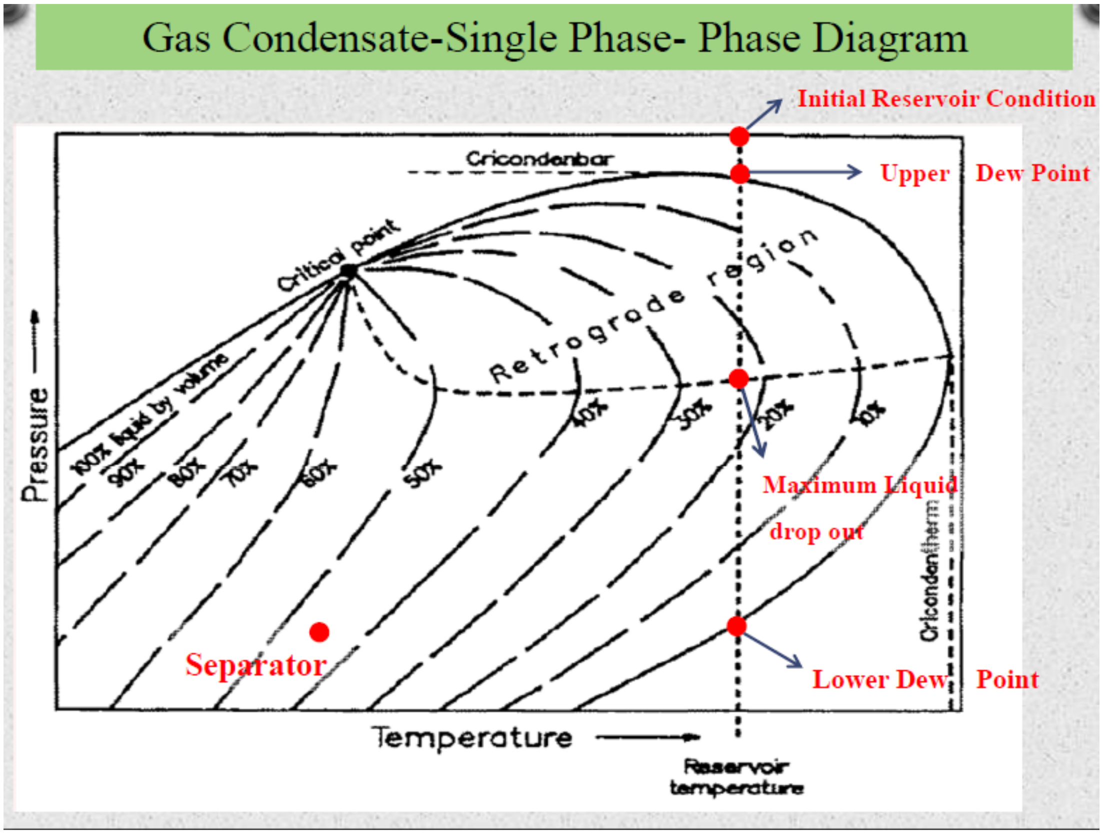
$$40 < API < 60$$

$$B_o \ ----- \ -$$

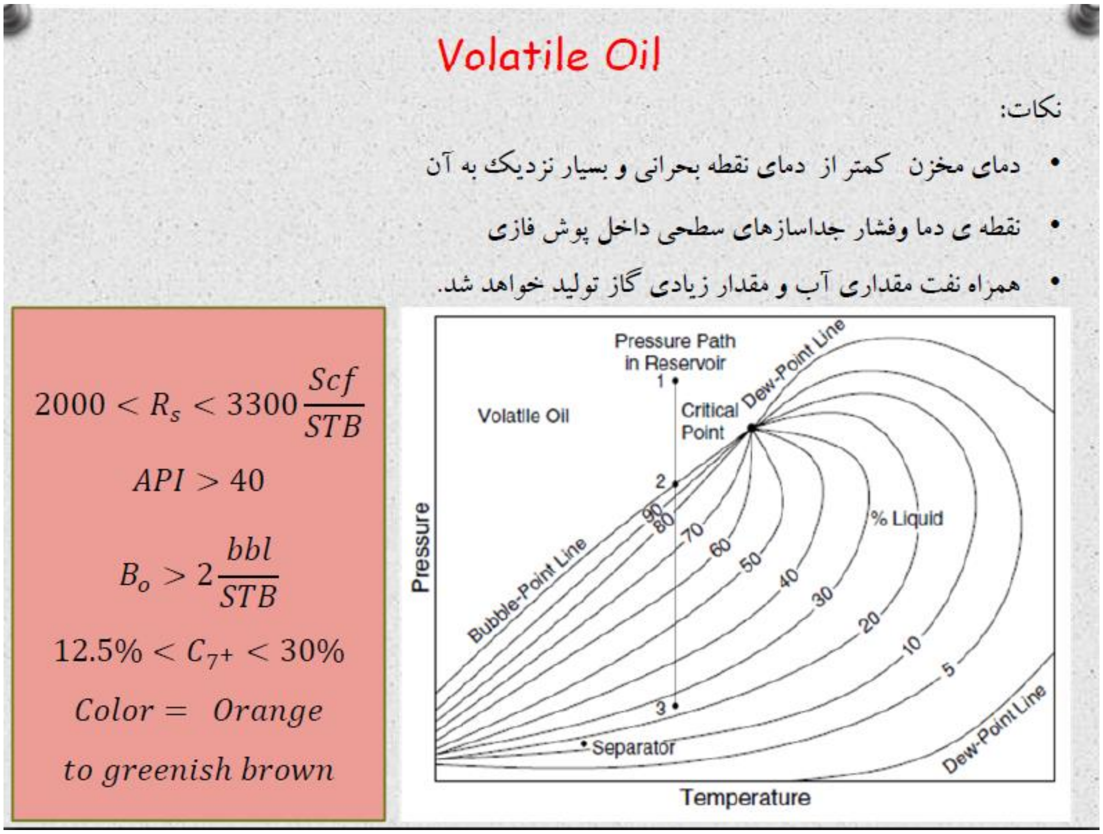
$$C_{7^+} < 12.5\%$$

$$Color = \ Lightly\ color$$

$$water\ white$$



Gas Condensate-Single Phase- Phase Diagram



Volatile Oil

نکات:

- دمای مخزن کمتر از دمای نقطه بحرانی و بسیار نزدیک به آن
- نقطه ی دما وفشار جداسازهای سطحی داخل پوش فازی
- همراه نفت مقداری آب و مقدار زیادی گاز تولید خواهد شد.

$$2000 < R_s < 3300 \frac{Scf}{STB}$$

$$API > 40$$

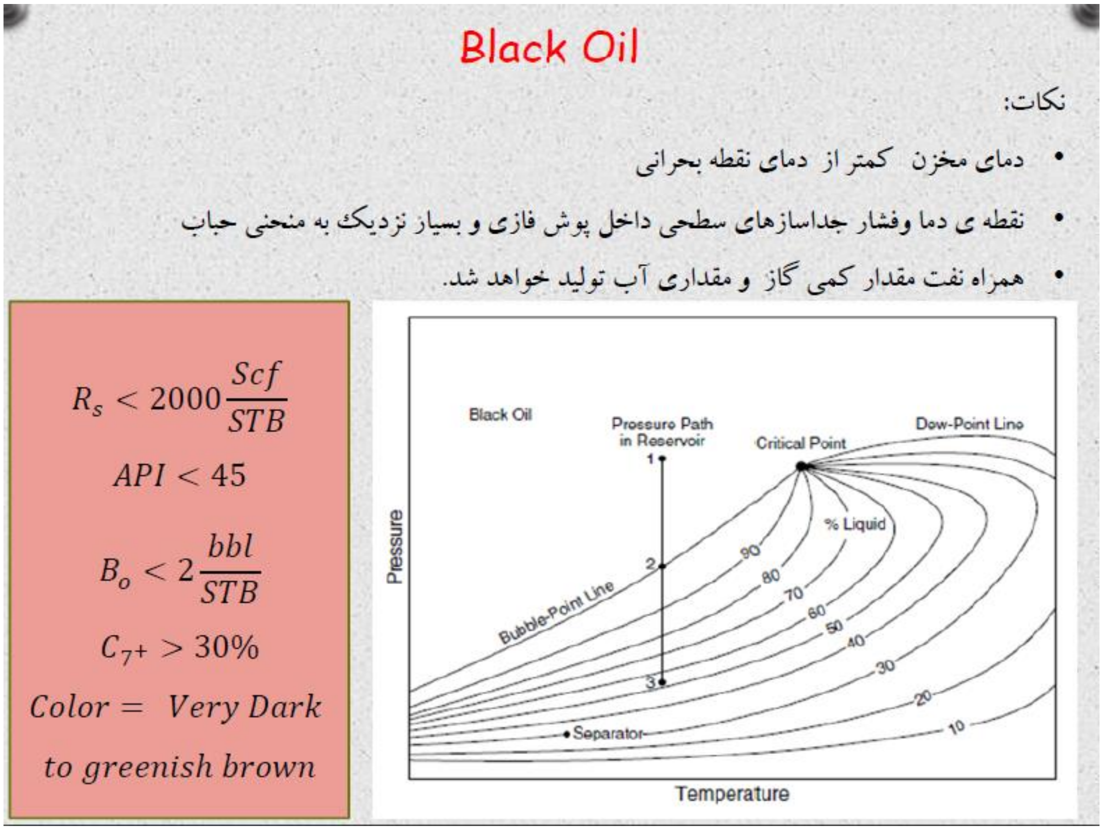
$$B_o > 2 \frac{bbl}{STB}$$

$$12.5\% < C_{7+} < 30\%$$

$$Color = \ Orange$$

$$to\ greenish\ brown$$

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 coloured 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.



Black Oil

نکات:

- دمای مخزن کمتر از دمای نقطه بحرانی
- نقطه ی دما وفشار جداسازهای سطحی داخل پوش فازی و بسیار نزدیک به منحنی حباب
- همراه نفت مقدار کمی گاز و مقداری آب تولید خواهد شد.

$$R_s < 2000\frac{Scf}{STB}$$

$$API < 45$$

$$B_o < 2\frac{bbl}{STB}$$

$$C_{7+} > 30\%$$

$$Color = \ Very\ Dark$$

$$to\ greenish\ brown$$