



SI Derived Units and Constants

| | | | | | |
|---|--|--|--|--------------------|---|
| $N = \frac{m \cdot kg}{s^2} = \frac{J}{m}$ | $J = \frac{m^2 \cdot kg}{s^2} = N \cdot m$ | $Pa = \frac{kg}{m \cdot s^2} = \frac{N}{m^2}$ | $W = \frac{m^2 \cdot kg}{s^3} = \frac{J}{s}$ | $Hz = \frac{1}{s}$ | $R = 459.67 + ^\circ F$ $K = 273.15 + ^\circ C$ $^{\circ}F = 1.8 ^\circ C + 32$ |
| Gas Constant = $8.314 \times 10^{-6} \text{ MPa} \cdot \text{m}^3/\text{mol K}$ | Water specific heat capacity = 4.184 kJ/kg K | Gas Constant = 8.314 J/mol K | | | |
| Gravitational Constant = 9.806 m/s^2 | Substance concentration = amount/volume | specific volume = $\rho^{-1} = \text{m}^3/\text{kg}$ | | | |

Important Definitions and Nomenclature

| | | | |
|---|--|--|---|
| Important Definitions | M = mass (kg) | N = number of moles (mol) | U = internal energy (J) |
| - Isolated system is not affected by changes in surroundings | V = volume (m ³) | P = absolute pressure (Pa) | G = Gibbs energy (J) |
| - Adiabatic system is thermally isolated from surroundings | H = enthalpy (J) | T = absolute temperature (K) | Q̇ = heat flow rate (J/s) |
| - Open system: mass can flow in and out of system | S = entropy (J/K) | W = work done on the system (J) | θ = property θ per unit mass |
| - Closed system: mass cannot flow in and out of system | R = gas constant | W _s = shaft work done on system (J) | θ = property θ per mole |
| - Steady-state : system properties do not change over time | C _v = constant volume molar heat capacity (J/mol K) | C _p = ideal gas molar heat capacity | M _k = mass flow rate at location k |
| - Isenthalpic : temperature is constant | C _p = constant pressure molar heat capacity | | |

Pure Substance Phase Behavior

Pure Substance Phase Diagram

Pressure vs. Temperature. Key points: TP (Triple Point), BP (Bubble Point), DP (Dew Point), CP (Critical Point).

Pressure - Volume Diagram

Pressure vs. Specific Volume. Key points: BP, DP, CP.

Lever Rule

$$x_L = \frac{\theta - \theta_v}{\theta_L - \theta_v}$$

$$x_L + x_v = 1$$

x_L = liquid phase mole fraction
 x_v = vapor phase mole fraction

θ and $\hat{\theta}$ can be any extensive property that's been converted to intensive

$$w_L = \frac{\hat{\theta} - \hat{\theta}_v}{\hat{\theta}_L - \hat{\theta}_v}$$

$$w_L + w_v = 1$$

w_L = liquid phase mass fraction
 w_v = vapor phase mass fraction

Conservation of Mass

General Balance Equation

$$\frac{d\theta}{dt} = (\text{Rate of } \theta) = (\text{Rate at Which } \theta \text{ Enters System}) - (\text{Rate at Which } \theta \text{ Leaves System}) + (\text{Rate at Which } \theta \text{ is Generated})$$

θ can be mass, moles, internal energy, or entropy
If θ is conserved quantity, generation term zero

Mass Balance Equation

$$\frac{dM}{dt} = \sum \dot{M}_k \text{ or } \frac{dN}{dt} = \sum \dot{N}_k \quad ; \quad M(t_2) - M(t_1) = \sum \Delta M_k$$

First Law of Thermodynamics

Energy Balance

First Law: Energy is Conserved

$$\frac{d}{dt} (\text{Energy of System}) = (\text{Rate of } \dot{Q} \text{ Energy In}) - (\text{Rate of } \dot{Q} \text{ Energy Out})$$

$$\frac{du}{dt} = \dot{Q} + \dot{W} + \sum \dot{M}_k \hat{h}_k \text{ or } \sum \dot{N}_k \hat{h}_k$$

Total Energy = $\frac{1}{2} M v^2 + Mgh + U$

Total Energy ≈ Internal Energy

Total work = shaft work + expansion work

Heat Capacity

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$\Delta U = N C_V \Delta T$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

$$\Delta H = N C_P \Delta T$$

Second Law of Thermodynamics

Entropy Balance

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \sum \dot{M}_k s_k + \dot{S}_{gen}$$

OR

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \sum \dot{N}_k s_k + \dot{S}_{gen}$$

T = temp at which heat flow takes place
 \dot{S}_{gen} = entropy generated within system

Second Law: Entropy can be created but not destroyed

$$\dot{S}_{gen} \geq 0$$

$\dot{S}_{gen} = 0$ if process reversible

At Equilibrium

$$\frac{dS}{dt} = 0 \quad \& \quad \dot{S}_{gen} = 0$$

Differential Entropy Change

For a closed system $du = Tds - PdV$ or $dU = TdS - PdV$

Free Energy and Reversibility

Free Energy

For a closed, isothermal, constant volume system

$$A = U - TS$$

A = Helmholtz energy

For a closed, isothermal, constant pressure system

$$G = U - TS + PV$$

G = Gibbs free energy

Can lose free energy by generating entropy

Entropy and Work

For a closed, constant T & V system

$$W_s = A_2 - A_1 + T \dot{S}_{gen}$$

For a closed, constant T & P system

$$W_s = G_2 - G_1 + T \dot{S}_{gen}$$

And if process reversible

$$W_s = A_2 - A_1 \quad \& \quad W_s = G_2 - G_1$$

If entropy generated, more work is required for a given change of state

$$W_s = W_s^{rev} + T \dot{S}_{gen}$$

Ideal Gas Properties

| | | | |
|----------------------------|--|--|--------------------------|
| Ideal Gas Law | Heat Capacity | Entropy | Fugacity |
| $PV = NRT$ | $C_p(T) = \frac{\partial H}{\partial T} = \frac{\partial(U+RT)}{\partial T}$ | $\Delta S = C_p \ln(T_2/T_1) + R \ln(V_2/V_1)$ | $f = P \quad \phi = 1$ |
| Z = 1 | $\Delta H = C_p \Delta T \quad \Delta U = C_v \Delta T$ | $\Delta S = C_p \ln(T_2/T_1) - R \ln(P_2/P_1)$ | f = fugacity |
| Z = compressibility factor | $C_p^* = C_p + R$ | $\Delta S = S_2 - S_1$ | φ = fugacity coefficient |
| | | | φ = f/P for all P & T |

Volumetric Equations of State

| | | | |
|---|--|--|--|
| Real Gas Law | van der Waals | Peng-Robinson (1978) | Redlich-Kwong-Soave |
| $PV = ZRT$ | $P = \frac{RT}{V-b} - \frac{a}{V^2}$ | $P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b^2(V-b)}$ | $P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$ |
| $Z = \frac{PV}{RT}$ | $b = \frac{1}{8} \frac{RT_c}{P_c}$ | $a(T) = 0.47524 \frac{R^2 T_c^2}{P_c} \alpha(T)$ | $a(T) = 0.42748 \frac{R^2 T_c^2}{P_c} \alpha(T)$ |
| $Z(T_r, P_r)$ | $a = \frac{27}{64} \frac{RT_c^3}{P_c}$ | $b = 0.0778 RT_c / P_c$ | $b = 0.08664 RT_c / P_c$ |
| $T_r = \frac{T}{T_c} \quad P_r = \frac{P}{P_c}$ | | $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$ | $\kappa = 0.48 + 1.574\omega - 0.176\omega^2$ |
| T_r = reduced temp P_r = reduced pressure | | If $\omega > 0.491 \quad \kappa = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.16666\omega^3$ | |

Equations of State Cubic Form

| | |
|--|--|
| $Z^3 + aZ^2 + bZ + c = 0$ | Work Flow |
| Dimensionless Parameters | - Find T_c, P_c , and ω |
| $\alpha = \frac{a}{RT} \quad \beta = \frac{bP}{RT} \quad \gamma = \frac{cP^2}{(RT)^2}$ | - Calculate a and b |
| | - Input T & P to calculate A and B |
| | - Determine α, β , and γ |
| | - Solve cubic equation for Z |
| | - the 3 roots: $Z_1 < Z_{unrav} < Z_2$ |
| | Z_v = vapor Z-factor |

Departure Functions

Departure Definition

$$H = H^{IG} + H^D$$

$$\Delta H = \Delta H^{IG} + H_2^D - H_1^D$$

$$\Delta H^{IG} = \int_{T_1}^{T_2} C_p^d dT - \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P} \right)_T dP$$

Enthalpy and Entropy Departure

$$H^D = \int_{P_1}^{P_2} \left[V - \left(\frac{\partial V}{\partial T} \right)_P \right] dP \rightarrow dP = \frac{1}{V} d(PV) - \frac{P}{V} dV \rightarrow H^D = RT(Z-1) + \int_{V_1}^{V_2} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

van der Waals EOS

$$H^D = RT(Z-1 - \frac{A}{Z})$$

Peng-Robinson Departure Functions

$$H^D = RT(Z-1) + \frac{T(da/dT) - a}{2b\sqrt{2}} \ln \left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right] \quad \frac{da}{dT} = -0.45724 \frac{R^2 T_c^2}{P_c} \frac{\alpha}{T_c}$$

$$S^D = R \ln(Z-B) + \frac{(da/dT)}{2b\sqrt{2}} \ln \left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right]$$

Phase Equilibrium and Fugacity

Equilibrium Criteria

Phase I & Phase II

$$N = N^I + N^{II} = \text{constant}$$

$$V = V^I + V^{II} = \text{constant}$$

$$U = U^I + U^{II} = \text{constant}$$

$P^I = P^{II} \quad T^I = T^{II}$

$G^I = G^{II}$

G must be minimum

Stability Criteria

$$C_V > 0 \quad \& \quad \left(\frac{\partial P}{\partial V} \right)_T < 0$$

must be satisfied in each phase

Gibbs Phase Rule

$$DF = C - PH + 2$$

DF = degrees of freedom
C = number of components
PH = number of phases

Fugacity

Gibbs free energy departure function

$$f = P \exp \left(\frac{G - G^{IG}}{RT} \right) = P \exp \left[\frac{1}{RT} \int_{P^0}^P \left(V - \frac{RT}{P} \right) dP \right] [=] P \alpha$$

$\phi = f/P$ = fugacity coefficient

$$\ln \phi = \left(\frac{1}{RT} \int_{P^0}^P \left(V - \frac{RT}{P} \right) dP \right) = \left(\frac{1}{RT} \int_{V^0}^V \left(\frac{RT}{V} - P \right) dV \right) - \ln Z + (Z-1)$$

van der Waals EOS $\ln \phi = (Z-1) - \ln(Z-B) - (A/Z)$

Fugacity coefficient: Peng-Robinson EOS

$$\ln \phi = (Z-1) - \ln(Z-B) - \frac{A}{2B\sqrt{2}} \ln \left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right]$$

p-vap Work Flow

- Follow steps from volumetric EOS section to calculate Z_v and Z_L

- Compute f^v and f^L by inputting Z_v and Z_L into above equations

- Iterate P until $f^v = f^L$

Mixtures

Multicomponent Equilibrium

$$f^I = f^{II} = f^{III} \quad f_i^I = f_i^{II} = f_i^{III} \dots$$

\hat{f}_i^I = fugacity of component i in phase I

Ideal Mixtures

Hydrocarbons make ideal mixtures

Volume and Enthalpy changes upon mixing are equal to zero

$$\Delta_{mix} V^{HM} = 0$$

$$\Delta_{mix} H^{HM} = 0$$

$G_i^{IM} = G_i + RT \ln x_i \quad f_i^{IM} = x_i f_i$

Equation of State Mixing Rules

$$a_{mix} = \sum_{i=1}^c \sum_{j=1}^c y_i y_j a_{ij}$$

$$b_{mix} = \sum y_i b_i \quad a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$$

k_{ij} = binary interaction parameter
 $k_{ij} = 0$ for HC-HC pairs

Liquefaction of Gas

Linde Process

Compressors and intercoolers (single or multistage) → Condenser → Throttling Valve → Vapor Drum → Gas

Flash Drum: Vapor (5) → Gas, Liquid (6) → Liquefied Gas

Total Work for Compression

$$-W_s = \dot{M}(\hat{h}_{in} - \hat{h}_{out}) \quad \& \quad \dot{S}_{in} = \dot{S}_{out}$$

Total work required for compression equals the summation of each stage

Fraction of Liquid Generated

$$\hat{h}_{in} = \hat{h}_{out} \quad \text{or} \quad \hat{h}_{in} = w_L^{out} \hat{h}_L + w_v \hat{h}_v$$

w_v = mass fraction of vapor
 w_L = mass fraction of liquid

$$w_L^{out} = \frac{\hat{h}_3 - \hat{h}_5}{\hat{h}_6 - \hat{h}_5} = \frac{\hat{h}_{in} - \hat{h}_v}{\hat{h}_L - \hat{h}_v}$$

Power Generation and Refrigeration Cycles

Rankine Cycle

High-pressure Steam → Turbine → Condenser → Pump → Boiler → High-pressure Water → Turbine

Refrigeration Cycle

Low-pressure Vapor → Compressor → Boiler → Valve → Condenser → High-pressure Liquid → Valve → Low-pressure Two phases → Compressor

Path

| Path | T | P | S | H | Energy Flow |
|------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|--|
| 1-2 | T ₁ , T ₂ | P ₁ , P ₂ | S ₁ , S ₂ | H ₁ , H ₂ | Ẇ _P = V̇ ₁ (P ₂ - P ₁) |
| 2-3 | T ₂ = T ₃ | P ₂ = P ₃ | S ₂ , S ₃ | H ₂ , H ₃ | Q̇ _B = H ₃ - H ₂ |
| 3-4 | T ₃ , T ₄ | P ₃ , P ₄ | S ₃ = S ₄ | H ₃ , H ₄ | Ẇ _T = H ₄ - H ₃ |
| 4-1 | T ₄ , T ₁ | P ₄ = P ₁ | S ₄ , S ₁ | H ₄ , H ₁ | Q̇ _C = H ₁ - H ₄ |

Coefficient of Performance

$$C.O.P. = \frac{Q_c}{W_c} = \frac{H_2 - H_3}{H_1 - H_2}$$

Low Pressure Approximations

Clausius-Clapeyron Equation

$$\ln \left(\frac{P_2^{vap}}{P_1^{vap}} \right) = -\frac{\Delta H^{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$\Delta H^{vap} = L_v$

ΔH^{vap} = enthalpy of vaporization
T = absolute temperature [=]K

Fugacity

$$f^L = P^{vap}$$

$$f^L = f^V$$

For a solid $f^S = P^{sat}$

Dalton's Law

$$P_i = y_i P$$

P_i = partial pressure
 x_i = liquid mole fraction
 y_i = vapor mole fraction

Raoult's Law

Valid if low P ideal mixture $x_i P_i^{sat} = y_i P$

$$K_i = \frac{P_i^{vap}}{P} \quad x_i = \frac{P - P_2^{vap}}{P_1^{vap} - P_2^{vap}}$$



Conversions and Constants

| | | | | | |
|--------------------|------------------|---|--------------------------------|------------------|------------------------------|
| 1 kPa = 0.1450 psi | 1 in = 2.54 cm | 1 acre = 43560 ft ² | 1 m ³ = 6.2898 bbl | R = 459.67 + °F | 1 lb _m = 453.59 g |
| 1 MPa = 10 bar | 1 ft = 0.3048 m | 1 m ² = 10.764 ft ² | 1 bbl = 5.6146 ft ³ | K = 273.15 + °C | 1 cp = 1 mPa·s |
| 1 atm = 14.696 psi | 1 mile = 5280 ft | 1 ft ³ = 7.4805 gal | 1 bbl = 42 US gal | °F = 1.8 °C + 32 | 1 BTU = 1.055 kJ |
| 1 atm = 1.013 bar | 1 mile = 1,609 m | | | | |

| | | |
|----------------------------------|---|---|
| Molar Mass of Air = 28.966 g/mol | Gas Constant = 10.732 psia · ft ³ /lbmol · R | Water density at SC = 62.37 lb _m /ft ³ |
| Standard Pressure = 14.696 psia | Gas Constant = 1.9859 BTU/lbmol · R | Molar Volume of ideal gas = RT ^{SC} /p ^{SC} |
| Standard Temperature = 60°F | V _M ^{SC} = 22.4 L/gmol @ 1.013 bar | V _M ^{SC} = 379.3 scf/lbmol @ 14.696 psia |

Reservoir Fluid Components

Major Components of Reservoir Fluids

Hydrocarbons

- 1. Paraffins
 - Saturated: Carbons have as many Hydrogens as possible
 - As carbon # increases, T_c increases and P_c slightly decreases
 - Waxes form when carbon # above C₂₀
 - Specific gravity = 0.65
- 2. Naphthenes/Cycloalkanes (C₅ - C₁₀₀)
 - Specific gravity = 0.88 - 0.9
- 3. Aromatics (C₆ - C₂₀)
 - Excellent solvents for dissolving Resins & Asphaltenes
 - Specific gravity = 0.88 - 0.9

Resins & Asphaltenes

- Complex, large molecules containing mainly C & H with S, O, or N
- Resins dissolve in petroleum but Asphaltenes do not dissolve (need aromatics)
- Resins and Asphaltenes increase the fluid's viscosity and determine its color

Composition of Reservoir Fluid

In general, as carbon number increases mole fraction decreases

Slope of line depends on fluid type

Pedersen et al (1983, 1984)

Mass and Mole Fraction Conversions

$$w_i = \frac{z_i MW_i}{\sum z_i MW_i}$$

$$z_i = \frac{w_i}{\sum w_i / MW_i}$$

w_i = mass fraction of component i n_T = total moles
MW_T = total molecular weight

Reservoir Fluid Properties

Reservoir Conditions

Surface Conditions

B_g Calculation

$$B_g = \frac{p_{sc} Z_{sc} T}{p T_{sc} Z} \left[\frac{R}{scf} \right]$$

Specific Gravity

$$\gamma_o = \left(\frac{\rho_o}{\rho_{sc}} \right)_{sc}$$

$$\gamma_g = \frac{MW_{air}}{MW_{gas}}$$

API Gravity

$$\gamma_{API} = 141.5 / \gamma_o$$

Compressibility

$$c = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \left[\frac{1}{psi} \right]$$

$$c_g = \frac{1}{p} - \frac{1}{z} \left(\frac{\partial z}{\partial p} \right)_T$$

$$c_o = -\frac{1}{B_o} \left(\frac{\partial B_o}{\partial p} \right)_T - B_g \left(\frac{\partial R_s}{\partial p} \right)_T$$

Fluid Properties - Pressure Dependence

z-Factor, B_g, R_s, B_o, BP vs Pressure (psi)

Phase Behavior

Clausius-Clapeyron

$$\frac{d \ln p^{vap}}{dT} = \frac{L_v}{T(V_{Mg} - V_{ML})}$$

Binary Mixtures

$$y_i = K_i x_i$$

$$z_i = x_i \bar{n}_i + y_i \bar{n}_v$$

Real Mixtures

If summation is equal to 1, pressure is at the bubble point or dew point

Flash Calculation

$$x_i = \frac{z_i}{\bar{n}_L + K_i(1 - \bar{n}_L)}$$

$$y_i = K_i x_i$$

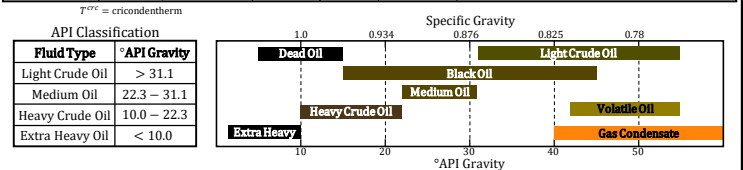
Ternary Diagrams

Diagram for a single pressure & temperature

Each corner represents 100% of that component and each leg signifies a binary mixture

Classification of Reservoir Fluids

| Fluid Type | T ^{RC} | Initial GOR scf/STB | Oil Gravity °API | Initial B _o RB/STB | C ₇₊ Fraction Mole % | Phase Behavior |
|---------------------------|----------------------------------|---------------------|------------------|-------------------------------|---------------------------------|---|
| Dry Gas | > T ^{RC} | -- | -- | -- | -- | Single phase at all pressures and temperatures |
| Wet Gas | > T ^{RC} | > 50,000 | -- | -- | -- | Gas phase in reservoir at all P & T. Separator within two-phase region. |
| Gas Condensate | T ^c - T ^{RC} | 3300 - 50000 | 40 - 60 | -- | < 12.5 | All gas initially. As pressure falls below dew point a liquid phase forms |
| Volatile Oil | < T ^c | 2000 - 3300 | 42 - 55 | 1.7 - 3.0 | 12.5 - 20 | T ^{RC} close to T ^c . Key difference between volatile and black oils is that the gas phase can produce liquid at surface. |
| Black Oil | < T ^c | 200 - 2000 | 15 - 45 | 1.1 - 1.7 | 25 - 50 | As reservoir pressure falls below bubble point, gas phase forms. |
| Undersaturated Oil | < T ^c | 200 - 2000 | 15 - 45 | 1.1 - 1.7 | 25 - 50 | Oil phase in reservoir at all P & T. Separator within two-phase region. |
| Dead Oil | < T ^c | -- | 5 - 15 | 1.0 - 1.1 | > 50 | Single phase at all pressures and temperatures. |



Z-Factor Approximation

Law of Corresponding States

$$P_{cp} = \sum y_i P_{c,i}$$

$$T_{cp} = \sum y_i T_{c,i}$$

Hall-Yarborough Correlation (1973)

$$t = (T_{pr})^{-1}$$

$$A = 0.06125 \left[\exp(-1.2(1-t)^2) \right]$$

$$B = 14.76t - 9.76t^2 + 4.58t^3$$

$$C = 90.7t - 242.2t^2 + 42.4t^3$$

$$D = 2.18 + 2.82t$$

$$f(x) = \frac{x + x^2 + x^3 - x^4}{(1-x)^3} - Ax - Bx^2 + Cx^3$$

set f(x) = 0 and solve for x

$$z = \frac{AP_{pr}}{x}$$

Properties of Brine

Ion Composition

Compressibility

$$c_w = B_w \frac{\partial}{\partial P} \left(\frac{1}{B_w} \right) = -\frac{1}{B_w} \left(\frac{\partial B_w}{\partial P} \right)_T = \frac{1}{\rho_w} \left(\frac{\partial \rho_w}{\partial P} \right)_T$$

Dissolved Solids

Stiff Diagram

Formation Water Analysis

Comparing diagram shapes can confirm reservoir communication, contamination of fresh water, or incursion of foreign water

Laboratory Measurements

Flash Vaporization Test

Differential Vaporization Test

Separator Test

Separator Test Results

Optimal Pressure

Standard pressure can be achieved because of the gas venting

$$B_{od} = \frac{\text{Liquid Vol. in cell}}{\text{Vol. at std. P\&T}} \left[\frac{RB}{bbl} \right]$$

$$R_{sb} = \frac{\text{Gas removed in scf}}{\text{Oil Vol. at std. P\&T}} \left[\frac{scf}{bbl} \right]$$

Developed Miscibility

Evolution of Developed Miscibility

Initial Oil, 2-phase region, Developed Miscibility

Injected gas and oil immiscible initially

Gas composition moves toward Plait Point

Developed miscibility (miscible displacement) can be achieved if the initial oil or injected gas composition is above the critical tie-line

Correcting Lab Measurements

Pressure Greater than Bubble Point

$$B_o = \left(\frac{V_T}{V_B} \right)_F B_{osb}$$

Pressure Equals BP

$$B_o = B_{osb}$$

Pressure Less than Bubble Point

$$B_o = B_{od} \left(\frac{B_{osb}}{B_{odb}} \right)$$