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

mnlotfollahi@yahoo.com

Home works: 1, 2, 3, 4, 5

Chapter 3: Phase Equilibria

Chapter 3: Phase Equilibria

در این فصل:

- مروری بر مفاهیم، تعاریف و روابط ترمودینامیکی مربوط به تعادلات سیالات
- بیان روش های مختلف برای تعیین تعادل و پیش بینی رفتار سیال به خصوص در حالت تعادل

منابع این فصل:

- Based on Chemical Engineering Thermodynamics (Van Ness)

You should know the thermodynamic properties based on the course of B.Sc. in thermodynamic II.

Chapter 3: Phase Equilibria

lefine a new function, viz. the original function, U, minus the product of the two quantities to be interchanged with due regard for the sign of the term in the original equation. That is, we define

$$H \equiv U-(-PV)=U+PV \qquad (2\text{-}7)$$

vhere H, the *enthalpy* of the system, is a state function because it is defined in terms of tate functions. Differentiation of Eq. (2-7) and substitution for dU in Eq. (2-3) gives

$$\boxed{dH = TdS + VdP} \qquad (2\text{-}8)$$

Similarly, to interchange T and S (but not P and V) in Eq. (2-3), we define the ***Helmholtz energy***

$$A \equiv U - TS \qquad (2\text{-}10)$$

giving

$$\boxed{dA = -SdT - PdV} \qquad (2\text{-}11)$$

and

In this case, the independent variables or constraints are T and V. Finally, to interchange both T and S and P and V in Eq. (2-3) so as to use T and P as the independent variables, we define the *Gibbs energy*

$$G \equiv U - TS - (-PV) = H - TS \qquad (2\text{-}13)$$

giving

$$\boxed{dG = -SdT + VdP} \qquad (2\text{-}14)$$

and

$$dG_{T,P} \le 0 \qquad (2\text{-}15)$$

Chapter 3: Phase Equilibria

Table 2-1 Some important thermodynamic relations for a homogeneous closed system.

Definition of *H*, *A*, and *G*

$$H = U + PV$$
$$A = U - TS$$
$$G = U + PV - TS = H - TS = A + PV$$

Fundamental Equations

$$dU = TdS - PdV \qquad dA = -SdT - PdV$$
$$dH = TdS + VdP \qquad dG = -SdT + VdP$$

Extensive Functions as Thermodynamic Potentials

$$dU_{S,V} \le 0 \qquad dA_{T,V} \le 0$$
$$dH_{S,P} \le 0 \qquad dG_{T,P} \le 0$$

Maxwell Relations Resulting from the Fundamental Equations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$
$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Identities Resulting from the Fundamental Equations

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$
$$\left(\frac{\partial U}{\partial S}\right)_V = T = \left(\frac{\partial H}{\partial S}\right)_P \qquad \left(\frac{\partial H}{\partial P}\right)_S = V = \left(\frac{\partial G}{\partial P}\right)_T$$
$$\left(\frac{\partial U}{\partial V}\right)_S = -P = \left(\frac{\partial A}{\partial V}\right)_T \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S = \left(\frac{\partial G}{\partial T}\right)_P$$

Heat Capacities

$$\left(\frac{\partial U}{\partial T}\right)_V = C_v \qquad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$$
$$\left(\frac{\partial H}{\partial T}\right)_P = C_p \qquad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$$

Chapter 3: Phase Equilibria

$$dH = TdS + VdP + \sum_i \mu_i dn_i \quad (2\text{-}21)$$

$$dA = -SdT - PdV + \sum_i \mu_i dn_i \quad (2\text{-}22)$$

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (2\text{-}23)$$

From the definition of μ_i given in Eq. (2-19) and from Eqs. (2-20) to (2-23), it follows that

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \quad (2\text{-}24)$$

Closed System: Single Phase: → Homogeneous

Multi Phase: → Heterogeneous

Chapter 3: Phase Equilibria

Chemical Potential

A closed system consisting of a number of phases in contact, called a heterogeneous closed system, can be treated as a collection of open systems, where each phase is considered to be a homogeneous one, exchanging mass with other open systems.

In an open system the change of Gibbs energy cannot be expressed by Eq.(3.6) as the energy can vary by components of the system crossing the phase boundary. Hence,

$$dG = -SdT + VdP + \sum_{i}^{N} (\partial G/\partial n_i)_{T,P,n_{j\neq i}} dn_i \qquad (3.13)$$

where n_i is the number of moles of each component, with the subscript n_j referring to all mole numbers except n_i, and N is the total number of components in the system.

The derivative of an extensive property relative to the number of moles of any component at constant pressure, temperature and other mole numbers, is defined as the partial molar property of that component. The partial molar Gibbs energy is called *chemical potential*, μ_i

$$\mu_i = (\partial G/\partial n_i)_{T,P,n_{j\neq i}} \qquad (3.14)$$

It can be shown [1], that,

$$\mu_i = (\partial G/\partial n_i)_{T,P,n_{j\neq i}} = (\partial A/\partial n_i)_{T,V,n_{j\neq i}} = (\partial H/\partial n_i)_{S,P,n_{j\neq i}} = (\partial U/\partial n_i)_{S,V,n_{j\neq i}} \qquad (3.15)$$

Open System:

$$dG = -SdT + VdP + \sum_i^N \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i$$

n_i: تعداد مول های هر جزء در سیستم

N: تعداد کل اجزاء سیستم

$i: \quad 1,2,\dots,N$

Partial Molar Property

خاصیت مولار جزئی:

مشتق جزئی هر کمیت مقداری، نسبت به تعداد مول ها در دما و فشار ثابت و هم چنین ثابت بودن تعداد مول های اجزاء دیگر

تعریف: انرژی گیبس مولی را پتانسیل شیمیایی می گویند:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{i\neq j}}$$

Chapter 3: Phase Equilibria

Fugacity

As relations amongst state properties are independent of the process path [2], Eq.(3.6) for a reversible process can be used to express the Gibbs energy change, hence, the chemical potential,

$$dG = -SdT + VdP \tag{3.21}$$

For a pure substance partial molar properties are the same as molar properties. Hence, the change of chemical potential of the pure substance i, is given by,

$$d\mu_i = dg_i = -s_i dT + v_i dP \tag{3.22}$$

where g, s and v are the molar Gibbs energy, molar entropy and molar volume respectively.

At constant temperature the above equation reduces to,

$$(\partial\mu_i / \partial P)_T = v_i \tag{3.23}$$

which leads to a simple expression for the chemical potential of an ideal gas, with the pressure-volume relation as,

$$Pv_i = RT \tag{3.24}$$

that is,

$$(\partial\mu_i / \partial P)_T = RT / P \tag{3.25}$$

where R is the universal gas constant.

یافتن اختلاف با حالت ایده آل

$$\mu_i - \mu_i^{ig} = RT\ln(f_i/P_i)$$

$$if \quad i = pure\ subtance \quad \rightarrow \quad \frac{f_i}{P_i} = \frac{f}{P}$$

$$\rightarrow \quad \emptyset = \frac{f}{P} \qquad fugacity\ coefficient$$

$$if \quad i = Component\ of\ Mixture \quad \rightarrow \quad \frac{f_i}{P_i} = \frac{f_i}{y_i P}$$

$$\rightarrow \quad \emptyset_i = \frac{f_i}{y_i P} \qquad Note \ : \ P \rightarrow 0 \quad \Rightarrow \quad \emptyset_i \rightarrow 1$$

مفهوم: اختلاف ضریب فوگاسیته از ۱ ، میزان انحراف از حالت ایده آل را برای یک سیستم غیر ایده آل نشان می دهد.

Chapter 3: Phase Equilibria

Integrating Eq.(3.25) at constant temperature, we obtain,

$$\mu_i - \mu_i^o = RT\ln(P/P^o) \tag{3.26}$$

The above equation provides a simple relation for the change of chemical potential of a pure ideal gas when its pressure changes from P^o to P isothermally.

Lewis [1] generalised Eq.(3.26) for application to real systems, by defining a "corrected pressure" function 'f', called *fugacity* (escaping tendency) as follows,

$$\mu_i - \mu_i^o = RT\ln(f_i/f_i^o) \tag{3.27}$$

where μ_i^o and f_i^o are the chemical potential and fugacity of the component i, respectively, at a reference state.

For an ideal gas, therefore, the fugacity is equal to its pressure, and the fugacity of each component is equal to its partial pressure.

The ratio of fugacity to pressure is defined as the fugacity coefficient ϕ. For a multicomponent system,

$$\phi_i = f_i/(Pz_i) \tag{3.28}$$

where z_i is the mole fraction of the component i. Since all systems behave as ideal gases at very low pressures,

$$\phi_i \to 1 \qquad \text{when} \qquad P \to 0 \tag{3.29}$$

The departure of fugacity coefficients from unity is, therefore, a measure of non-ideality of the system.

Writing Eq.(3.27) for the component i, in each phase of a heterogeneous system, with all reference states at the same temperature, the equality of the chemical potential at equilibrium given by Eq.(3.20), leads to,

$$f_i^{(1)} = f_i^{(2)} = f_i^{(3)} = \ldots = f_i^{(\theta)} \qquad i=1,2,\ldots N \tag{3.30}$$

Multi Component System

$$\ln\varnothing_i = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{i\neq j}} - \frac{RT}{V}\right]dV - \ln Z \qquad i = 1,2,\ldots,N$$

V: *Total Volume* $\qquad n = \sum n_i$

Z: *Compressibility factor for mixture* $\qquad Z = PV/nRT$

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The fugacity coefficient of a pure compound can be determined by incorporating Eq.(3.32) into the general expression for the fugacity coefficient, Eq.(3.31),

$$\ln\phi = \int_0^P \left(\frac{Z-1}{P}\right)dP = (Z-1) - \ln Z + \frac{1}{RT}\int_\infty^v \left(\frac{RT}{v} - P\right)dv \qquad (3.35)$$

where v is the molar volume. Depending on the form of the equation of state, one of the above two expressions for the fugacity can be simpler to use.

Example 3.1.

The compressibility factor of a pure gas at 290 K can be related to its pressure as,

$$Z = 1 - 6.5\times10^{-2}P - 7.5\times10^{-4}P^2 \qquad P<15 \text{ MPa}$$

where P is in MPa. Calculate the gas fugacity at 10 MPa.

Solution:

Substituting the above expression of Z in Eq.(3.35), we obtain,

$$\ln\phi = \int_0^P \left(\frac{Z-1}{P}\right)dP = \int_0^P \left(\frac{-6.5\times10^{-2}P - 7.5\times10^{-4}P^2}{P}\right)dP$$

$$\ln\phi = \left[-6.5\times10^{-2}P - 7.5\times10^{-4}P^2/2\right]_0^{10} = -0.6875$$

ϕ=0.5028

f=$\phi\times$P=5.028 MPa

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Ex 3-1 Gas (pure component)

$$z = 1 - 6.5 * 10^{-2}P - 7.5 * 10^{-6}P^2$$

$$f\Big|_{@\ P=10\,MPa} = ?$$

$$ln\emptyset = \int_0^P \left(\frac{Z-1}{P}\right) dP$$

Solution

$$\rightarrow \quad ln\emptyset = \int_0^{10} -6.5 * 10^{-2} - 7.5 * 10^{-6}P \ = \ -0.6875$$

$$\rightarrow \quad \emptyset = 0.5028$$

$$\rightarrow \quad f = \emptyset * P = 0.5028 * 10 = 5.028\, MPa$$

Chapter 3: Phase Equilibria

3.2 EQUILIBRIUM RATIO

Let us consider two phases of liquid, L, and vapour, V, at equilibrium. Eq.(3.30) for such a system is,

$$f_i^L = f_i^V \qquad i=1,2,...N \qquad (3.40)$$

Applying Eq.(3.28) to both phases, we obtain:

$$f_i^L = x_i P \phi_i^L \qquad i=1,2,...N \qquad (3.41)$$

$$f_i^V = y_i P \phi_i^V \qquad i=1,2,...N \qquad (3.42)$$

Hence,

$$K_i \equiv y_i / x_i = \phi_i^L / \phi_i^V \qquad i=1,2,...N \qquad (3.43)$$

where K_i is called the equilibrium ratio and is defined as the ratio of mole fraction of component i in the vapour phase y_i, to that in the liquid phase x_i. A general and rigorous approach to determine the fugacity coefficient of a component in both phases from volumetric information, using an equation of state, is given in Chapter 4.

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Assuming that the vapour is an ideal gas, we obtain,

$$f_{i,pure}^{V} = P \tag{3.48}$$

The effect of pressure on fugacity of a condensed phase at low pressure is small [1] and can be neglected. The fugacity of a pure liquid at low pressure can, therefore, be assumed equal to its fugacity at the saturation pressure. The fugacities of saturated vapour and liquid are equal, as the two phases are at equilibrium. Furthermore, the vapour fugacity at low pressure can be assumed equal to its pressure. Hence, the liquid fugacity can be taken equal to the vapour pressure of the substance at the prevailing temperature,

$$f_{i,pure}^{L} = P_i^s \tag{3.49}$$

where P_i^s is the saturation (vapour) pressure of the pure compound, i.

Substituting Eqs.(3.48) and (3.49) into Eq.(3.47), we obtain,

$$y_i P = x_i P_i^s \tag{3.50}$$

or

$$K_i = P_i^s / P \tag{3.51}$$

Eq.(3.51) is known as Raoult's law. Considering the above assumptions, it is only valid at low pressure for simple mixtures.

معادله ویریال

$$z = 1 + \frac{BP}{RT}$$ بر حسب فشار

نکته: ضریب دوم معادله ویریال (B) فقط تابعی از دما است.

$$ln\emptyset = \int_0^P \left(\frac{Z-1}{P}\right) dP = \int_0^P \frac{B}{RT} dP \quad \rightarrow \quad ln\emptyset = \frac{BP}{RT}$$

$$z = 1 + \frac{B}{V} + \frac{C}{V^2}$$ بر حسب حجم

$$ln\emptyset = z - 1 - lnz - \int_V^\infty \frac{(z-1)dV}{V} = \frac{2B}{V} + \frac{\left(\frac{B}{2}\right)C}{V^2} - lnz$$

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Henry's Law

The proportionality of component fugacity to its concentration, as assumed in Eq.(3.45) is valid for components at low concentrations in most liquid mixtures,

$$f_i = H_i x_i \tag{3.52}$$

where H_i is called *Henry's constant*, which is experimentally determined.

The concentration of component, i, is generally expected to be less than 3 mole % for the above equation to be valid [1]. It is, therefore, a useful equation to determine the solubility of hydrocarbons in water where the solubility is generally low.

At low pressure, where the assumption of ideal gas is valid, Eq.(3.48) can be used to describe fugacities in the gas phase,

$$Py_i = H_i x_i \tag{3.53}$$

which is known as Henry's law. Hence,

$$K_i = H_i/P \tag{3.54}$$

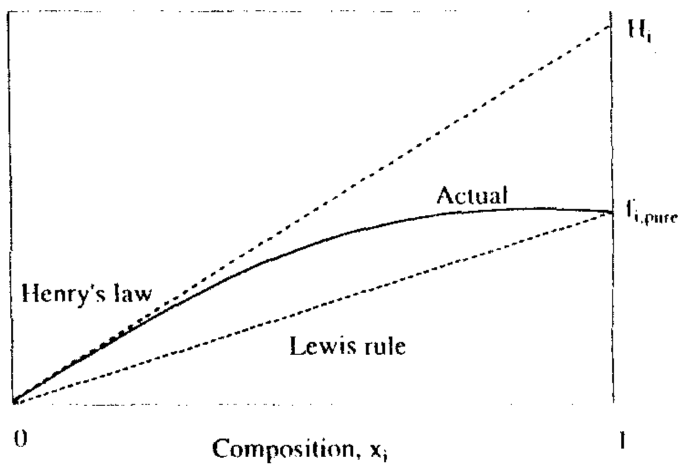

Figure 3.1. Comparison of Henry's law with Lewis rule.

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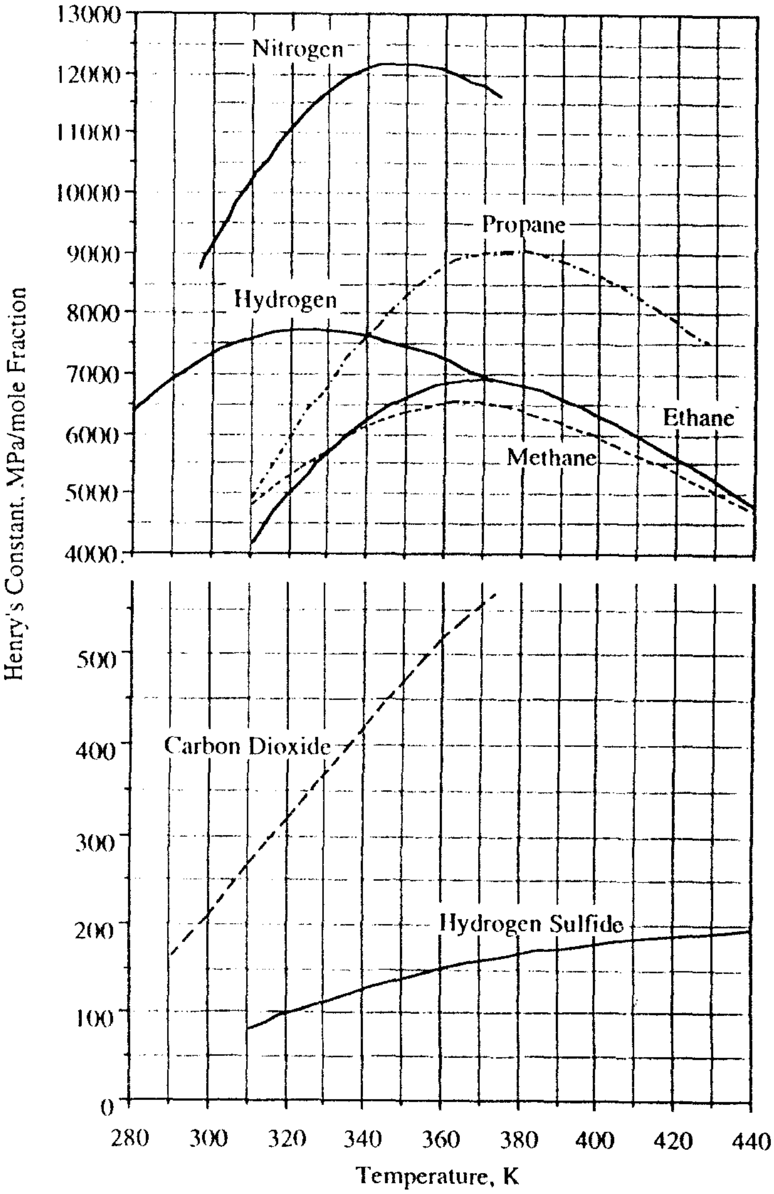


Figure 3.2 Henry's constants for solubility of hydrocarbons in water. Reprinted with permission [6], Copyright (1953) American Chemical Society.

وابستگی ثابت هنری به فشار

Krichevsky-Kasarnovsky Equation:

به سختی توسط روابط ترمودینامیکی تعیین می گردد

$$H_i = H_i^0 \exp\left[\frac{V_i^{\infty}(P - P^0)}{RT}\right]$$

$H_i^0 \quad @ \quad P^0$

V_i^{∞} → حجم مولی جزء i در حلال در رقت بینهایت

در محدوده فشار سیستم و ترکیبات آن، ثابت در نظر گرفته می شود.

مقادیر متوسط V_i^{∞}

Component	V_i^{∞} ($\frac{cm^3}{g.mole}$)
N_2	35
C_1	40
C_2	55
C_3	88

نکته:

1. اطلاعات کمی در مورد V_i^{∞} مربوط به اجزاء در آب موجود است.
2. V_i^{∞} با دما تغییر می کند.
3. V_i^{∞} در نزدیکی نقطه بحرانی به فشار وابسته می گردد.

The dependency of Henry's constant on pressure can be determined rigorously by thermodynamic relations as,

$$H_i = H_i^o \exp[v_i^\infty (P - P^o)/RT] \qquad (3.55)$$

where H_i^o is Henry's constant at P^o, and v_i^∞ is the partial molar volume of component i in the solvent at infinite dilution, assumed constant over the prevailing pressure and composition ranges. Eq.(3.55) is known as the Krichevsky-Kasarnovsky equation [5].

Limited information on v_i^∞ of compounds in water are available in the literature [6]. The partial molar volume varies with temperature, and becomes pressure dependent near the critical point. An average value of 35, 40, 55, and 80 cm^3/gmol, can be used for nitrogen, methane, ethane, and propane respectively.

Example 3.3.

Estimate the solubility of methane in water at 373 K, and 65 MPa using Henry's law. Compare the result with the value shown in Figure 2.28.

Solution:

The Henry's constant for methane at 65 MPa is calculated from Eq.(3.55):

At T=373 K, $H^o=6.5\times10^3$ MPa/mol fraction (Figure 3.2), and P^o=0.10 MPa.

$H_{C1}=(6.5\times10^3$ MPa/mol fraction) exp[$(40\times10^{-3}m^3/kgmol)\times(65.00-0.10)$MPa/

$(0.0083144\times373$ MPa.m^3/kgmol)] $=1.4378\times10^4$ MPa/mol fraction.

The solubility of methane is calculated using Eq.(3.52),

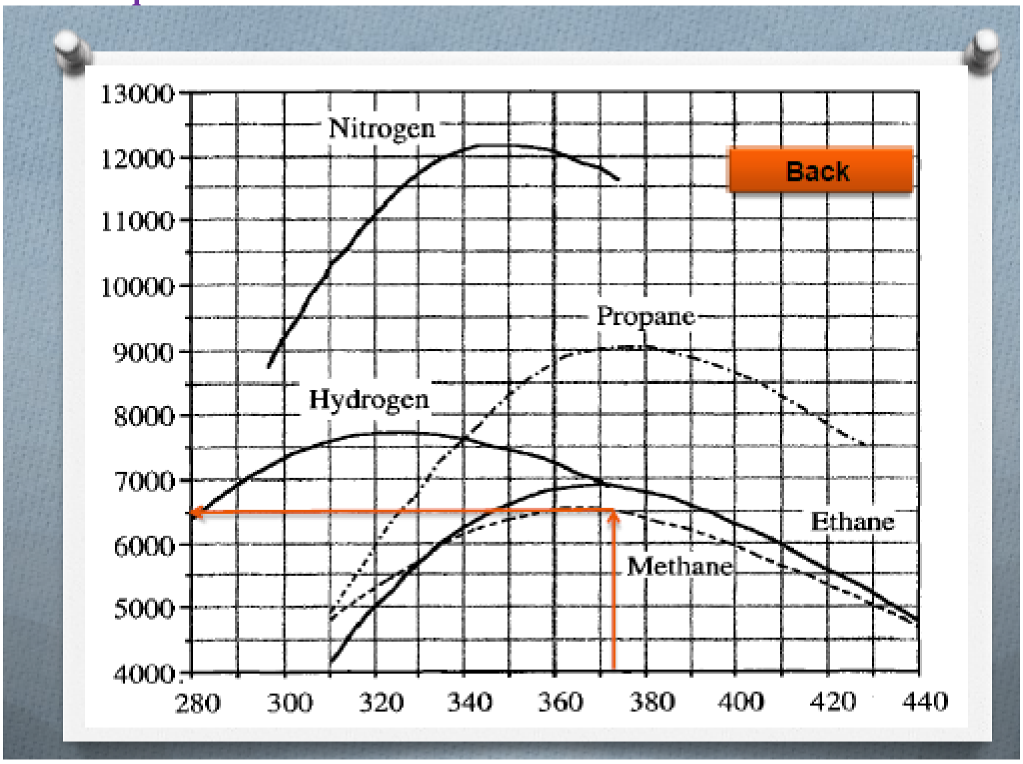
$$f_{C1}^V = Py_{C1}\phi_{C1}^V = H_{C1}x_{C1}$$

The gas can be assumed as pure methane due to low volatility of water relative to methane: $y_{C1}=1$. The fugacity coefficient of methane vapour at the prevailing conditions can be calculated by an equation of state as applied in Example 4.1. Assuming $\phi_{C1}^V=1$, we obtain,

$f_{C1}^V=P=65$ MPa= $(1.4378\times10^4$ MPa/mol fraction) $\times x_{C1}$

$x_{C1}=4.52\times10^{-3}$ mole fraction of methane in water.

The solubility value is read from Figure 2.28 equal to 4.3×10^{-3}.



$\rightarrow \quad f_{C1}^{V} = P = 65\ MPa = 1.4378 * 10^{4}\, x_{C1}$

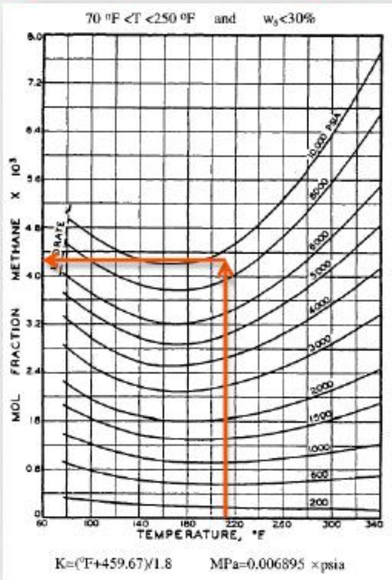
$\rightarrow \quad x_{C1} = 4.52 * 10^{-3} \quad mole\ fraction\ of\ C1\ in\ water$

مقایسه با شکل ۲-۲۷ حلالیت متان در آب

$373\ °K = 211°F$

$65\ MPa \cong 9426\ Psi$

From figure solubility is equal to 4.3×10^{-3}



نکته: در مثال 4-1 با استفاده از معادله واندروالس حلالیت متان به دست آمده است:

$\emptyset = 0.987 \approx 1$

$\rightarrow \quad x_{C1} = 4.42 * 10^{-3}$

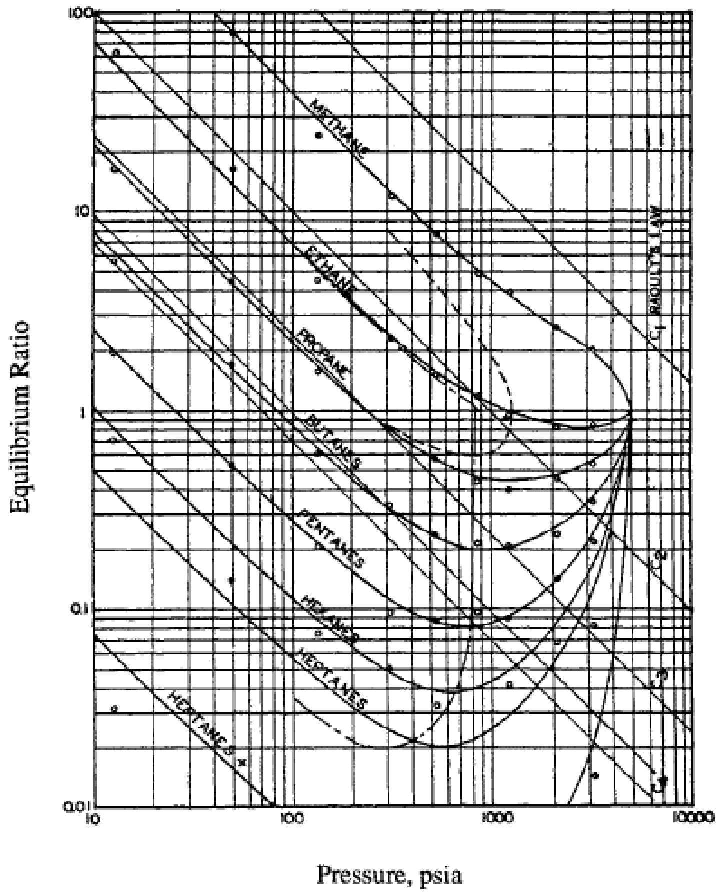


Figure 3.3. Equilibrium ratios of a hydrocarbon mixture at 322 K (120°F). SPE-AIME Copyright. Reproduced from [7] with permission.

Standing [12], represented the graphical correlation of Mathews, Roland, and Katz [13] as,

$$T_{c,C_{7+}} = 338 + 202 \times \log(M_{C_{7+}} - 71.2) + (1361 \times \log M_{C_{7+}} - 2111)\log S_{C_{7+}} \quad (3.57)$$

$$P_{c,C_{7+}} = 8.191 - 2.97 \times \log(M_{C_{7+}} - 61.1) + (S_{C_{7+}} - 0.8)[15.99 - 5.87 \times \log(M_{C_{7+}} - 53.7)] \quad (3.58)$$

where T_c, and P_c are in K and MPa, respectively.

Other correlations to estimate the critical properties of the C_{7+} fraction are also available [14,15].

توضیح: برای حدس ترکیبات فاز مایع، به عنوان حدس اولیه از ترکیبات خوراک مورد نظر می باشد.

نکته: محاسبات بر مبنای weighted average صورت می گیرد.

$$w_i = \frac{x_i M_i}{\sum x_i M_i}$$ → برای Tc و Pc

محاسبات مربوط به تعادلات فازی در فصل پنجم (بخش ۱) توضیح داده خواهد شد.

در محاسبات فشار همگرایی ← برای تخمین $C7^+$ ← Matthews/Roland/Katz

$$T_{c_{C7+}} = 338 + 202 * \log(M_{C_{7+}} - 71.2) + (1361 * \log M_{C_{7+}} - 2111) \log S_{C_{7+}}$$

$$P_{c_{C7+}} = 8.191 - 2.97 \times Log(M_{C_{7+}} - 61.1) + (S_{C_{7+}} - 0.8)[15.99 - 5.87 \times \text{Log}(M_{C_{7+}} - 53.7)]$$

T: °K

P: MPa

Sutton & Whitson

نوع دیگر محاسبات مربوط به C_7^+ در کتاب McCain بر اساس Sg و دمای جوش(T_b) از معادله Lee-Kesler قرار داده شده است.

Lee-Kesler:

$$P_{Pc} = \exp[8.3634 - \frac{0.0566}{\gamma_{c^{7+}}} - \left(0.24244 + \frac{2.2898}{\gamma_{c^{7+}}} + \frac{0.11857}{\gamma^{c7+2}}\right)10^{-3}T_B + \left(1.4685 + \frac{3.648}{\gamma^{c7+}} + \frac{0.47227}{\gamma^{c7+2}}\right)10^{-7}{T_B}^2 - \left(0.42019 + \frac{1.6977}{\gamma^{c7+2}}\right)10^{-3}{T_B}^3]$$

$$T_{Pc} = 341.7 + 811\gamma_{c^{7+}} + (0.4244+0.1174\gamma_{c^{7+}})\, T_B + \frac{(0.4669-3.2623\gamma_{c^{7+}})10^5}{T_B}$$

$$Whitson \rightarrow T_B = [4.5579{M_{c^{7+}}}^{0.15178}{\gamma_{c^{7+}}}^{0.15427}]^3$$

Back

Standing:

Note 1:

$$T_{c_{C7+}} = 338 + 202 \times \log(M_{C_{7+}} - 71.2) + (1361 \times \log M_{C_{7+}} - 2111) \log S_{C_{7+}}$$

Note 2:

$$P_{c_{C7+}} = 8.191 - 2.97 \times Log(M_{C_{7+}} - 61.1) + (S_{C_{7+}} - 0.8)[15.99 - 5.87 \times Log(M_{C_{7+}} - 53.7)]$$

$$\begin{cases} T_c = 642.35\ K\ (696.5\ ^0F) \\ P_c = 2.173\ MPa\ (315.2\ psig) \end{cases} \rightarrow \textit{Pseudo Heavy Component is slightly}$$

Chapter 3: Phase Equilibria

حالت قبلی → $K = f(T, P, Comoposition)$

Standing

مقادیر آزمایشگاهی K را که توسط معادلات Hoffmann ارائه شده بود را به یکدیگر مرتبط نمود.

$$\log(KP) = \eta' + \beta'[\alpha'\left(\frac{1}{T_b} - \frac{1}{T}\right)] \qquad \alpha' = \frac{\log\left(\frac{P_c}{P_a}\right)}{\frac{1}{T_b} - \frac{1}{T_c}}$$

$$\eta' = -0.96 + 6.53 \times 10^{-2} \times P + 3.16 \times 10^{-4} \times P^2 \qquad Table\ 3-1$$

$$\beta' = 0.890 - 2.46 \times 10^{-2} \times P - 7.36 \times 10^{-4} \times P^2 \qquad P_a = 0.1\ MPa$$

Standing [16] correlated the experimental K-values of Oklahoma City crude oil/natural gas samples generated by Katz and Hachmuth [17], using Eq.(3.59) proposed by Hoffmann et al. [18].

$$\log KP = \eta' + \beta' [\alpha' ({}^{1}/T_b - {}^{1}/T)] \qquad (3.59)$$

$$\eta' = -0.96 + 6.53 \times 10^{-2} P + 3.16 \times 10^{-3} P^2 \qquad (3.60)$$

$$\beta' = 0.890 - 2.46 \times 10^{-2} P - 7.36 \times 10^{-4} P^2 \qquad (3.61)$$

where P is pressure in MPa, and T_b (normal boiling point) and T are in K. α' is the slope of the straight line connecting the critical point and the boiling point at atmospheric pressure, P_a, on a log vapour pressure vs. $(T)^{-1}$ plot.

$$\alpha' = [\log(P_c / P_a)] \Big/ [1/T_b - 1/T_c] \qquad (3.62)$$

The values of α' and T_b for C_{7+} fractions can be obtained from:

$$\alpha' = 563 + 180n - 2.364n^2 \qquad (3.63)$$

$$T_{bn} = 167 + 33.25n - 0.539n^2 \qquad (3.64)$$

where n is the number of carbons of the normal paraffin that has the same K-value as that of the C_{7+} fraction. It can be estimated by comparing the molecular weight of the C_{7+} fraction with those of normal paraffins, Table A.1 in Appendix A. Standing correlated n for the Oklahoma City crude oil samples by,

$$n = 3.85 + 0.0135T + 0.2321P \qquad (3.65)$$

where T is in K and P is in MPa.

Chapter 3: Phase Equilibria

Table 3.1.
Values of α' and T_b for use in Standing's equilibrium ratio correlation.

Compound	α', K	T_b, K
Nitrogen	261	61
Carbon Dioxide	362	108
Hydrogen Sulphide	631	184
Methane	167	52
Ethane	636	168
Propane	999	231
iso-Butane	1132	262
n-Butane	1196	273
iso-Pentane	1316	301
n-Pentane	1378	309
iso-Hexanes	1498	335
n-Hexane	1544	342
Hexanes (lumped)	1521	339
n-Heptane	1704	372
n-Octane	1853	399
n-Nonane	1994	424
n-Decane	2127	447

Chapter 3: Phase Equilibria

Wilson [20] proposed the following equation to estimate the equilibrium ratio below 3.5 MPa (500 psia):

$$K_i = (P_{ci}/P)\exp[5.37(1+\omega_i)(1-T_{ci}/T)] \qquad (3.66)$$

where ω is the acentric factor and T_c and P_c are the absolute critical temperature and pressure respectively. The Wilson equation basically uses Raoult's law, with the vapour pressure related to the critical properties using the definition of the acentric factor, Eq.(1.9).

Wilson (@ low pressures)

$P < 3.5\ MPa\ (500\ psia)$

$$K_i = \frac{P_{ci}}{P}\exp\left[5.37\,(1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right]$$

Wilson used ***Raoult's law***

$$\omega = -\log\left(\frac{P^{sat}}{P_c}\right)\Big|_{T_r=0.7} - 1.0$$

The Wilson equation generally provides reliable estimation of K-values for sub-critical components, but overestimates those of the supercritical components [24]. The equation has been extended to higher pressures [22] as,

$$K_i = (P_{ci}/P_k)^{A-1}(P_{ci}/P)\exp[5.37A(1+\omega_i)(1-T_{ci}/T)] \qquad (3.67)$$

where

$$A = 1-[(P-P_a)/(P_k-P_a)]^n$$

and P_k is the convergence pressure, as correlated by Standing [12],

$$P_k = 0.414M_{C_{7+}} - 29.0 \qquad (3.68)$$

where P_k is in MPa. The exponent n varies between 0.5 and 0.8, depending on the fluid, with a default value of 0.6.

Modified Wilson

$$K_i = \left(\frac{P_{ci}}{P_K}\right)^{A-1}\left(\frac{P_{ci}}{P}\right)\exp[5.37A\,(1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)]$$

$$A = 1-\left[\frac{P-P_a}{P_k-P_a}\right]^n$$

$0.5 < n < 0.8$

$default:\quad n = 0.6$

$P_k = 0.414\,Mw_{C7+} - 29$ *(Convergence Pressure)* *(Standing)*

The convergence pressure for the modified Wilson equation is calculated from Eq.(3.68), equal to 57.94 MPa, with the value of A=0.644.

The calculated equilibrium ratios using the Standing method, K_s, the Wilson equation, K_w, and the modified Wilson equation, K_{mw}, are compared with the experimental values, K_e, in the following table.

Component	α', K	T_b, K	K_S	K_W	K_{mW}	K_e
Equation			3.59	3.66	3.67	
C_1	167	52	3.4601	4.1626	4.6099	3.0022
C_2	636	168	1.1454	0.6666	1.4170	1.0274
C_3	999	231	0.5490	0.1731	0.5947	0.4749
iC_4	1132	262	0.3245	0.0693	0.3298	0.2855
nC_4	1196	273	0.2727	0.0499	0.2669	0.2268
iC_5	1316	301	0.1686	0.0207	0.1517	0.1353
nC_5	1378	309	0.1478	0.0162	0.1292	0.1091
C_6	1521	339	0.0874	0.0057	0.0661	0.0539
C_{7+}	2214	460	0.0088	0.0000	0.0005	0.0086

Note that although the pressure is above the working range of the Standing correlation, it predicts the results more reliably than others. The modification has improved the Wilson equation in general, except for predicting the equilibrium ratio of methane.

Example 3.5.

Estimate equilibrium ratios of the gas-oil system described in Example 3.4, using the Standing method and the Wilson equation. Compare the results with the experimental values.

Solution:

The critical properties of C_1-C_6 are read from Table A.1 in Appendix A. The properties of C_{7+} are calculated as follows.

Standing Correlation

Substituting the pressure and temperature in Eq.(3.65), the equivalent carbon number of C_{7+} is determined equal to 10.66, which results in α'=2213 K and T_b=460.2 K, using Eq.(3.63) and Eq.(3.64), respectively.

The coefficients of Eq.(3.59) at 10.45 MPa are calculated as,

η'= 0.067465, using Eq.(3.60)

β = 0.5526, using Eq.(3.62)

The results are given in the following table.

Wilson Equation

The estimation of critical properties of a pseudo component, using its specific gravity and molecular weight, is described in Section 6.2. A simple approach is to represent C_{7+} with a normal alkane with the same molecular weight. In this case, C_{15}, with a molecular weight of 212 is considered to represent C_{7+}. The critical properties of C_{7+} are, therefore, estimated equal to T_c=708 K, P_c=1.480 MPa, and ω=0.6863.

Ex 3-5: Estimate K for Ex 3-4 →
- Standing Method
- Wilson Equation

P = 10.45 MPa
T = 325 °K

Solution

نکته: می توان K را از نمودار های مربوط به فشار همگرایی نیز به دست آورد.

در Ex 3-4 فشار بالا بود: 10 MPa

Standing → Intermediate Pressures : P<7MPa (1000psia)

$$\log(KP) = \eta' + \beta'[\alpha'\left(\frac{1}{T_b} - \frac{1}{T}\right)]$$

$$\eta' = -0.96 + 6.53 \times 10^{-2} \times P + 3.16 \times 10^{-4} \times P^2$$

$$\beta' = 0.890 - 2.46 \times 10^{-2} \times P - 7.36 \times 10^{-4} \times P^2$$