CHE 415
Chemical Engineering
Thermodynamics II

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Phase Equilibrium and Fugacity

Learning Objectives for today's lecture

- At the end of this week's lecture, you should be able to:

  - Derive expression for fugacity and fugacity coefficient

  - Application of fugacity to phase equilibria and their calculations.

FUGACITY, FUGACITY COEFFICIENT

- [ ] From the Gibbs free energy differential,
- [ ]   dG = VdP – SdT   6-1
- [ ] Applied to 1 mole of pure fluid i at constant T, this equation becomes,
- [ ] $dG_i = V_i dP$ (const. T)   6-2
- [ ] For an ideal gas, $V_i = RT/P$
- [ ] Thus, $dG_i = RT\dfrac{dP}{P}$
- [ ] or $dG_i = RT\ dlnP$ 6-3
- [ ] Eqn.6-3 can be made universally valid by replacing P with a new function known as fugacity, f
- [ ] Eqn.6-3 becomes,
- [ ] $dG_i = RT\ dln f_i$ (const. T)   6-4
- [ ] Where f_i, called the fugacity of pure i, is a property of I with the units of pressure.
- [ ] For the special case of an ideal gas,
- [ ] $RT\ dln f_i = RTdlnP$
- [ ] Integration gives,
- [ ] $ln f_i = lnP + lnC$

FUGACITY, FUGACITY COEFFICIENT

- [ ] and $\qquad f_i = \text{CP}$
- [ ] Where C is a constant
- [ ] Putting C = 1, makes fugacity = pressure
- [ ] Since ideality is assumed as P➤0, then the equation
- [ ] $$\lim_{P \to 0} \frac{f_i}{P} = 1 \qquad \text{is valid} \qquad\qquad 6\text{-}5$$
- [ ] The fugacity $\widehat{f_i}$ of a component in a solution is similarly defined as
- [ ] $$d\overline{G_i} = RT d\ln \widehat{f_i} \quad \text{(const. T)} \qquad\qquad 6\text{-}6$$
- [ ] For $\qquad \lim_{P \to 0} \dfrac{\widehat{f_i}}{x_i P} = 1$
- [ ] Thus for a mixture of gases,
- [ ] $$\widehat{f_i} = x i P \qquad\qquad \text{(ideal gas)}$$
- [ ] The product $x_i P$ is known as the partial pressure P$_i$ of component *i* in the gas mixture.
- [ ] i.e. P$_i = x_i P$
- [ ] and $\qquad \sum P_i = \sum x_i P = P \sum x_i = P$
- [ ] i.e the pressure of a gas mixture is equal to the sum of the partial pressures of its individual components.

FUGACITY COEFFICIENT

❑ The fugacity coefficient is defined as the ratio of the fugacity of a material to its pressure. For a pure substance,

❑ $$\varphi_i = \frac{f_i}{P}$$ 6-7

❑ For a component in solution,

❑ $$\widehat{\varphi_i} = \frac{\widehat{f_i}}{x_i P}$$ 6-8

❑ φ_i is the fugacity coefficient and is dimensionless.
❑ Values of φ_i and $\widehat{\varphi_i}$ are readily calculated from PVT data

❑ **Derivation of f_i and φ_i.**
❑ From eqn.6-4
❑ $\qquad\qquad dG_i = RT\ d\ln f_i \quad$ (const. T)
❑ At constant T and composition (x), 1 mole of solution, the equation
❑ $$d(nG) = -(nS)dT + (nV)dP + \sum[\mu_i]dn_i$$
❑ Becomes $\qquad dG_i = V_i dP \qquad\qquad$ (const. T,x) $\qquad$ 6-9
❑ Combination of eqns.6-4 and 6-9 gives,
❑ $\qquad\qquad RT\ d\ln f_i = V_i dP$ 6-10
❑ A logarithmic differentiation of 6-7 gives

FUGACITY COEFFICIENT

❑ A logarithmic differentiation of 6-7 gives

❑ $$d\ln f_i = d\ln\varphi_i + d\ln P$$

❑ $$= d\ln\varphi_i + \frac{dP}{P}$$

❑ Substituting into eqn. 6-10 gives

❑ $$d\ln\varphi_i = \frac{PV_i}{RT}\frac{dP}{P} - \frac{dP}{P} \qquad \text{(const. T,x)} \qquad 6\text{-}11$$

❑ Since, $Z_i = \frac{PV_i}{RT}$, we have

❑ $$d\ln\varphi_i = (Zi - 1)\frac{dP}{P} \qquad \text{(const. T,x)} \qquad 6\text{-}12$$

❑ Integrating between P = 0, where $\varphi_i = 1$ and P gives

❑ $$\ln\varphi_i = \int_0^P (Zi - 1)\frac{dP}{P} \qquad\qquad 6\text{-}13$$

❑ Since $f_i = \varphi_i P$, the corresponding expression for $\ln f_i$ is

❑ $$\ln f_i = \ln P + \int_0^P (Zi - 1)\frac{dP}{P} \qquad \text{(const. T,x)} \qquad 6\text{-}14$$

❑ Analogous equations to 6-13 and 6-14 for which V rather than P is the variable of integration are easily derived. They are

❑ $$\ln\varphi_i = (Z_i - 1) - \ln Zi - \int_0^V (Z_i - 1)\frac{dV_i}{V} \qquad 6\text{-}15$$

❑ $$\ln f_i = \ln\frac{RT}{V_i} + (Z_i - 1) - \int_0^V (Zi - 1)\frac{dV_i}{V} \qquad 6\text{-}16$$

FUGACITY COEFFICIENT

- For ideal gases, Z = 1, hence,
- $$\varphi_i = \varphi = 1$$
- and $f_i = f = P$
- The analogous equation for a component i of an ideal gas mixture (solution) are
- $$\widehat{\varphi_i} = \varphi = 1$$
- and $\hat{f}_i = y_iP$ 6-17
- Where yi is the mole fraction of component I in a gas phase.
- Since the residual volume is related to the compressibility factor by the expression
- $$\Delta V_i = \frac{RT}{P}(1 - Z_i)$$ 6-18
- Hence eqn.6-13 becomes,
- $$\ln\varphi_i = -\frac{1}{RT}\int_0^P (\frac{RT}{P} - Vi\,)\,dP$$
- $$= -\frac{1}{RT}\int_0^P \Delta V_i\,dP \qquad \text{(const. T)}$$ 6-19
- Also the expression
- $$\ln\widehat{\varphi_i} = \int_0^P (\widehat{Z}_i - 1)\frac{dP}{P} \qquad \text{(const. T,x) is valid}$$ 6-20

FUGACITY COEFFICIENT

- ❑ And since $\widehat{Z}_i = \dfrac{PV_i}{RT}$

- ❑ $\qquad \ln\widehat{\varphi_i} = -\dfrac{1}{RT}\int_0^P (\dfrac{RT}{P} - \bar{V}_i)\,dP \qquad$ (const. T,x) $\qquad$ 6-21

- ❑ The generalized correlation for fugacity coefficient, φ is

- ❑ $\qquad \ln\varphi = \dfrac{P_r}{T_r}(\beta^0 + \omega\beta^1) \qquad$ (const. T,x) is valid

- ❑ Applicable to non-polar or slightly polar gases, where β^0 and β^1 are given by

- ❑ $\qquad\qquad\qquad \beta^0 = 0.083 - \dfrac{0.422}{T_r^{1.6}}$

- ❑ And $\qquad\qquad \beta^1 = 0.139 - \dfrac{0.172}{T_r^{4.2}}$

- ❑ And also $\qquad \ln\varphi = ln\varphi^0 + \omega ln\varphi^1$ or $\varphi = \varphi^0\varphi^{1^{\omega}}$

- ❑ Where $\varphi^0, \varphi^1, \beta^0, \omega\ and\ \beta^1$ are functions of (P_r,T_r) found in literature (see <u>Lee-Kesler chart</u>).

- ❑ Practice Example.
- ❑ Determine the values of φ and f for n-butane gas at 460K and 15atm by the generalized correlation for fugacity coefficient. (P_C = 37.5atm, T_C = 425.2K, ω = 0.193)
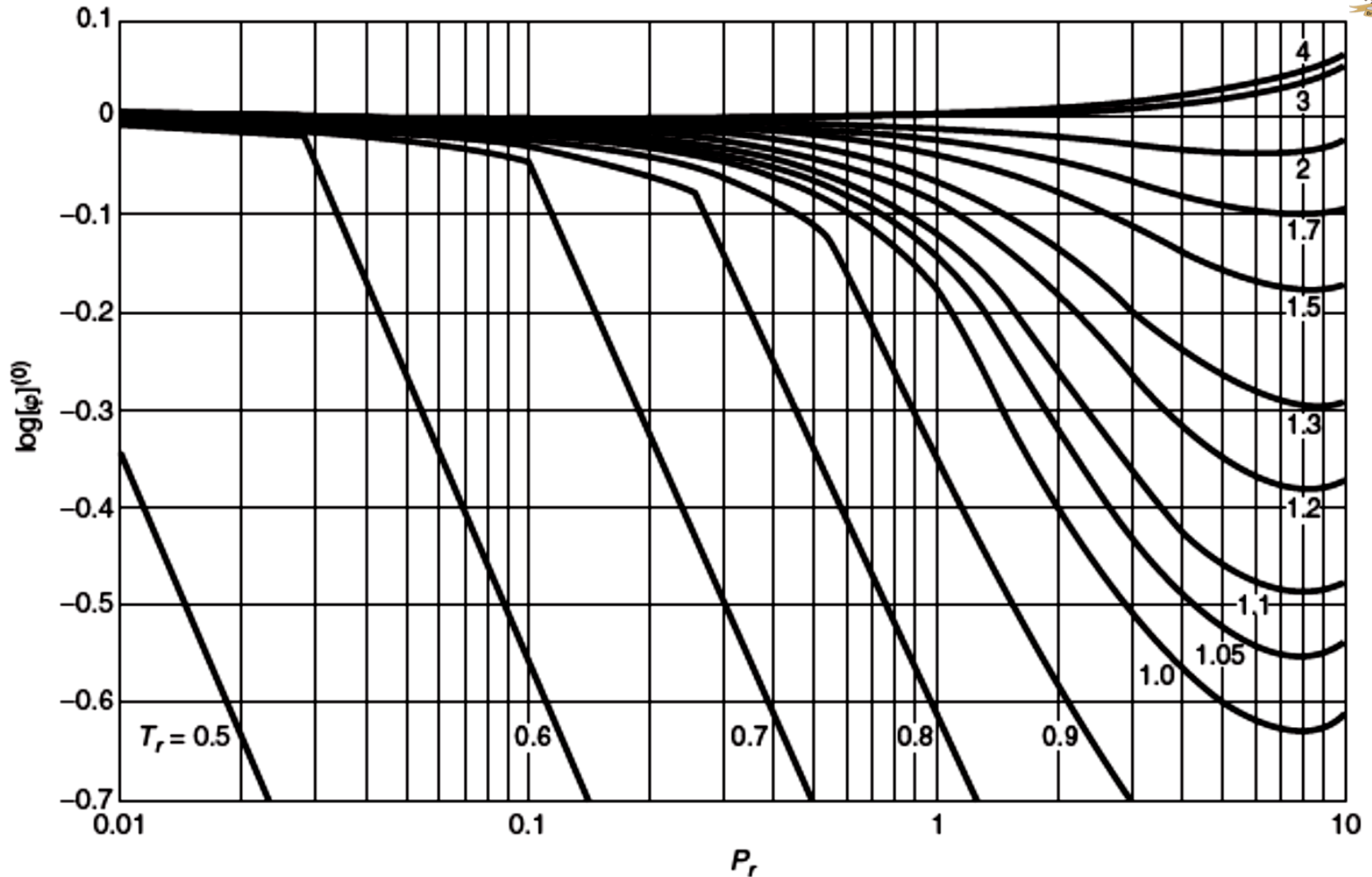
Figure 7.1 Corresponding states correlation for the fugacity coefficient in reduced coordinates—simple fluid term. Based on the Lee–Kesler equation of state.
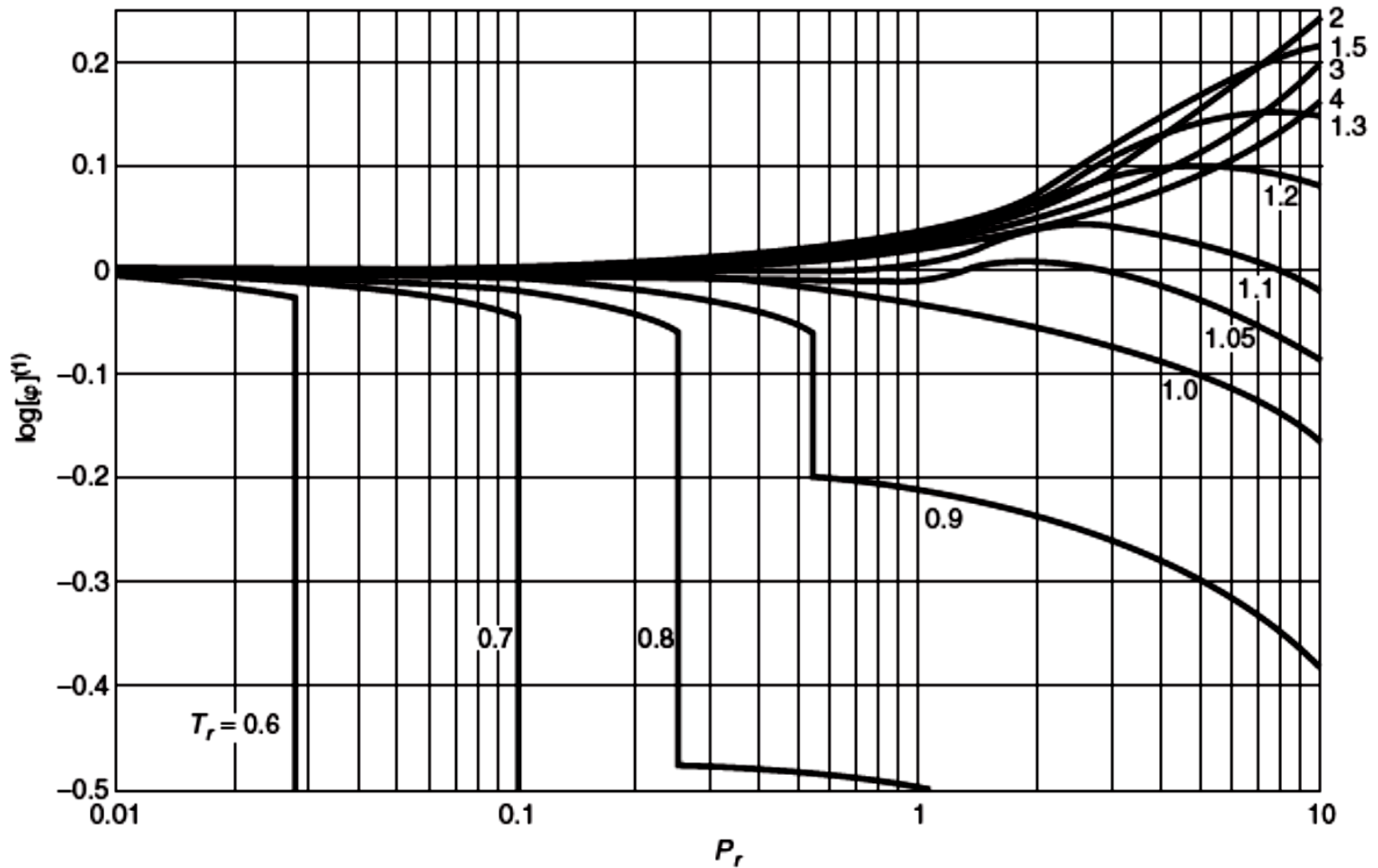
Figure 72 Corresponding states correlation for the fugacity coefficient in reduced coordinates—correction term. Based on the Lee–Kesler equation of state.

SOLUTION

- We know that
- $$\ln\varphi = \frac{P_r}{T_r}(\beta^0 + \omega\beta^1) \qquad \text{(const. T,x)}$$
- And $$P_r = \frac{P}{P_C} = \frac{15}{37.5} = 0.40$$
- $$T_r = \frac{T}{T_C} = \frac{460}{425.5} = 1.08$$
- $$\beta^0 = 0.083 - \frac{0.422}{1.08^{1.6}} = -0.290$$
- And $$\beta^1 = 0.139 - \frac{0.172}{1.08^{4.2}} = 0.014$$
- Substituting in the equation above
- $$\ln\varphi = \frac{0.40}{1.08}(-0.290 + (0.193)(0.014)$$
- $$= \text{-0.1064}$$
- And $$\varphi = e^{\text{-0.1064}}$$
- $$= 0.899$$
- Since $f = \varphi P$
- $$= 0.899 \times 15$$
- $$= 13.49 \text{ atm}$$

EQUALITY OF FUGACITY AS A CRITERION OF PHASE EQUILIBRIUM

❑ The concept of fugacity as the criterion for chemical equilibria is as that of using chemical potential. To derive this relationship for fugacity, we begin by equating the chemical potentials of phases α and β:

$$\mu_i^\alpha = \mu_i^\beta \qquad \text{6-22}$$

❑ Also fugacity as defined by G.N. Lewis is given by the relation

❑ $$\mu_i - \mu_i^o \equiv RT \ln\left[\frac{\hat{f}_i}{\hat{f}_i^o}\right] \qquad \text{6-23}$$

❑ Combining eqn.6-22 and 6-23 yields,

$$\mu_i^{\alpha,o} + RT \ln\left[\frac{\hat{f}_i^\alpha}{\hat{f}_i^{\alpha,o}}\right] = \mu_i^{\beta,o} + RT \ln\left[\frac{\hat{f}_i^\beta}{\hat{f}_i^{\beta,o}}\right]$$

❑ Applying a mathematical relationship to the quotient in the logarithms and rearranging gives:

$$\mu_i^{\alpha,o} - \mu_i^{\beta,o} = RT \ln\left[\frac{\hat{f}_i^{\alpha,o}}{\hat{f}_i^{\beta,o}}\right] + RT \ln\left[\frac{\hat{f}_i^\beta}{\hat{f}_i^\alpha}\right]$$

EQUALITY OF FUGACITY AS A CRITERION OF PHASE EQUILIBRIUM

❑ The first three terms are just a restatement of Eqn.6-22; hence the remaining term must be equal to zero, that is,

$$0 = RT \ln \left[\frac{\hat{f}_i^\beta}{\hat{f}_i^\alpha} \right]$$

❑ Or $\boxed{\hat{f}_i^\alpha = \hat{f}_i^\beta}$ 6-24

❑ Eqn.6-24 forms the criterion for chemical equilibrium in terms of fugacity. It is just as simple as that for chemical potential.

THANK YOU FOR YOUR ATTENTION! ANY QUESTIONS?