Chapter 9 – Phase Equilibria for pure fluids
(Gibbs Energy and Fugacity)

9.1 – 9.4 Phase equilibria without values for G

9.5 Introduction of fugacity as an alternative to G

9.5– 9.6 Calculation of $f/P = \varphi$

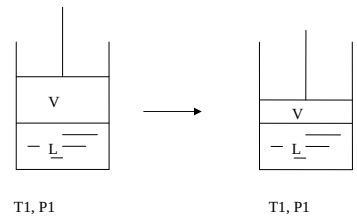
9.7 f for gases

9.8 f for liquids

9.9 f for solids

9.10-9.11 saturation from EOS, choosing stable roots

9.1 – Proof that G determines phase equilibria



Boundary around V + L

$d\underline{G} = -\underline{S}\, dT + \underline{V}\, dP$ (1)

Also, $dG^V = -S^V\, dT + V^V\, dP$ (2)

and $\underline{G} = n^v G^v + n^L G^L$ (3)

prd rule on (3)

Use (2)

Use mass balance

Gibbs energy is the appropriate quantity to use to determine phase equilibria.

Note: ΔH^{vap} and ΔS^{vap} are related

9.2 Claperyon and Clausius Claperyon

Along sat curve

$$dG^V = -S^V\, dT + V^V\, dP$$
$$dG^L = -S^L\, dT + V^L\, dP$$

Equating

Clapeyron Equation

$$\frac{dP^{sat}}{dT} = \frac{S^V - S^L}{V^V - V^L} = \frac{H^V - H^L}{T(V^V - V^L)} \qquad 9.6$$

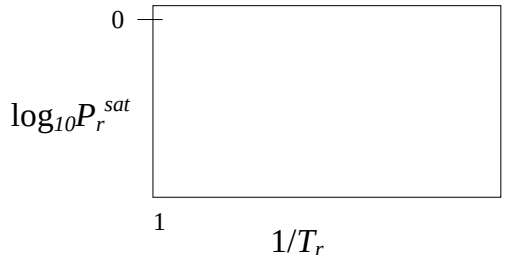
$$d\ln P^{sat} / d(1/T) = -\Delta H^{vap} / (R\Delta Z) \qquad 9.7$$

Clausius – Clapeyron Equation

$$d \ln P^{sat} / d(1/T) = -\Delta H^{vap} / R \qquad \text{(ig 9.8)}$$

<u>9.3 Shortcut Estimation of Psat</u>

Plot of $\ln P^{sat}$ vs. 1/T (or $\ln P_r^{sat}$ vs. $1/T_r$)



$\log_{10} P^{sat} = m\,(1/T_r - 1)$

Evaluate using definition of acentric factor

Shortcut estimate (good to about $T_r = 0.5$)

Correlation of P^{sat} - Antoine Equation

Requires fitting of A, B, C. Use care when extrapolating!

Methods to quantify Gibbs departure

9.4 Changes in G with P, changes in $(G-G^{ig})$ with P
9.5 Definition of *f* as an alternative to $(G-G^{ig})$
9.6 use of *f* as a criteria for phase equilibria

9.4 Changes in G with P

$dG = -SdT + V\,dP$

for ideal gas: dG^{ig}

for real fluid: dG =

changes in departure:
$dG - dG^{ig} =$

Evaluation of departure:

9.5 definition of *f* as an alternative to $(G-G^{ig})$

Chemical engineers find it convenient to define a new property, fugacity, to use instead of $(G-G^{ig})$. The fugacity will be easier to estimate 'off the cuff' than the Gibbs departure, and will be equivalent. We will build on work here in chap 9-13.

For an ideal gas, $dG^{ig} = V^{ig}dP = RT/P\,dP = RT\,d\ln P$

Define a new property, fugacity, f, that also varies as the ln:

Thus,
$d(G - G^{ig}) = RT\,(d\ln f - d\ln P) = RT\,d\ln(f/P)$

Thus

9.6 Fugacity as a criteria for phase equilbria

$G^V = G^L$

Water vapor is nearly an ideal gas at 100C and 1.013bar, where water vapor and liquid coexist at the normal boiling point.
What is f^V? What is f^L?

9.7 Calculation of *f* for non-ideal GASES

General Method

$$\ln \varphi = \int_0^p \frac{(Z-1)}{P} dP = \int_0^V \frac{(Z-1)}{\rho} d\rho + Z - 1 - \ln Z$$

Equations of State:

1. Virial – Z = 1 + BP/RT

B depends on T only, given in chapter 7.

2. Peng-Robinson or other cubic or more complex EOS.

$$\ln \varphi = \int_0^V \frac{(Z-1)}{\rho} d\rho + Z - 1 - \ln Z \text{, becomes}$$

$$\ln \varphi = -\ln(Z-B) - \frac{A}{B\sqrt{8}} \ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right] + Z - 1 \quad \text{(example 8.6!)}$$

3. Generalized Charts

9.8 Calculation of *f* for LIQUIDS

1. Poynting method

Uses three steps

a. use any vapor method to get $f^{satV} = \varphi^{sat} P^{sat}$ at saturation.

b. $f^{satL} = f^{satV} = \varphi^{sat} P^{sat}$

c. add <u>Poynting correction</u> relative to saturation:

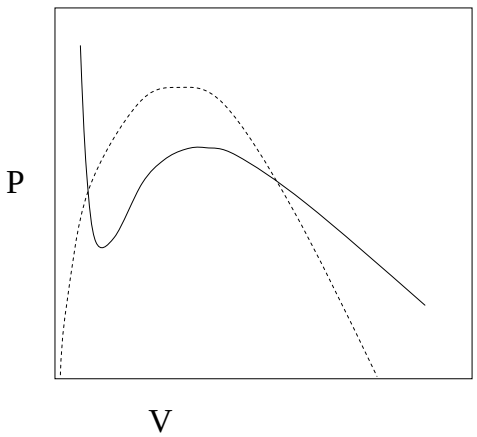
integrating

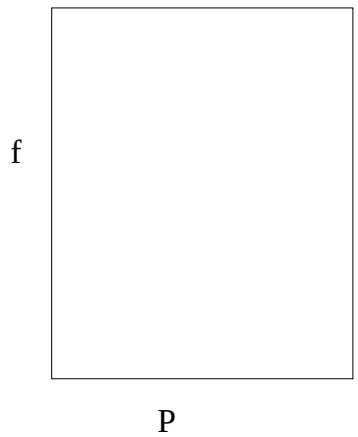
$$f^L = f^{sat} \exp\left[\frac{V^L(P-P^{sat})}{RT}\right] = \varphi^{sat} P^{sat} \exp\left[\frac{V^L(P-P^{sat})}{RT}\right]$$

often the Poyting correction is neglected:
when nearly an ideal gas at saturation,

Estimate f^L for water exiting a condenser at 0.02 MPa.

2. Equation of State Method (Peng Robinson)





9.9 Calculation of f for SOLIDS

almost always Poynting method.

$$f^L = f^{sat} \exp\left[\frac{V^L(P - P^{sat})}{RT}\right] = \varphi^{sat} P^{sat} \exp\left[\frac{V^L(P - P^{sat})}{RT}\right]$$

Psat almost always low, nearly an ideal gas at saturation,

9.10 Saturation Conditions from an EOS

PREOS examples, review how to find P^{sat} or T^{sat}