1)

For a pure gas at some T and P, the fugacity $f_i^V = \phi \mathbf{P}$

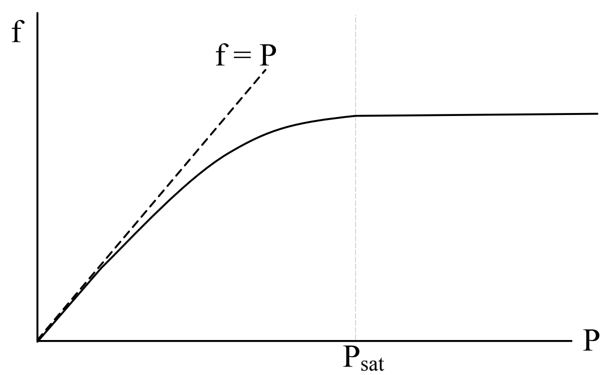
where ϕ is fugacity coefficient, which is a measure of deviation from **ideal gas** behavior.

For a pure liquid at some T and P, $f_i^L = \boldsymbol{\phi_i^{sat} P_i^{sat} \exp[V_i^L (P - P_i^{sat})/RT]}$

where the last term is called the Poynting factor.

What about a pure solid at some T and P? $f_i^S = \boldsymbol{\phi_i^{subl} P_i^{subl} \exp[V_i^S(P - P_i^{subl})/RT]}$

2) Sketch the curve of f vs. P for a pure component at constant T where P^{sat} = the liquid-vapor saturation pressure at T.



3) Fugacity is some "fictitious pressure"; can we say fV = RT? Why or why not?

No. Although fugacity is a measure of deviation from ideal gas behavior, it is not a "replacement pressure."

3) Consider liquid water at 100°C. What is the pressure at which the fugacity is 10% higher than the fugacity at P^{sat}?

If you went to the recitation section, you should see that this is just figuring out when the Poynting correction = 1.1.

$\boldsymbol{\exp[V_i^L (P - P_i^{sat})/RT] = 1.10}$

$\boldsymbol{V_i^L \approx (1\ g/cm^3)^{-1} (1\ mol/18\ g) (10^{-6}\ m^3)/(1\ cm^3)}$ **R = 8.314 J/mol K** **T = 373 K** $\boldsymbol{P_i^{sat} = 1}$ **atm.**

Solve for P. P = 165 atm.

4) Complete the following table

	Pure Gas	**Gas Mixture**	**Liquid Solution**
Fugacity	$f_i = \phi P$	$\hat{f}_i = \hat{\phi}_i y_i P$	$\hat{f}_i = \gamma_i x_i P_i^{sat} \phi_i^{sat}$
Coefficients and G	$\ln \phi = G^R / RT$	$\ln \hat{\phi}_i = \bar{G}_i^R / RT$	$\ln \gamma_i = \bar{G}_i^E / RT$
Total G	$G^R = RT \ln \phi$	$G^R = \sum_i y_i \bar{G}_i^R$ $G^R = \sum_i y_i RT \ln \hat{\phi}_i$	$G^E = \sum_i y_i \bar{G}_i^E$ $G^E = \sum_i x_i RT \ln \gamma_i$
Gibbs-Duhem	N/A	$\sum_i y_i \, d(\ln \hat{\phi}_i) = 0$	$\sum_i x_i \, d(\ln \gamma_i) = 0$
Special cases	$\phi = 1$ for ideal gas (low pressure)	$\hat{\phi}_i = 1$ for ideal gas mixture (low pressure)	$\gamma_i = 1$ for ideal solutions and when $x_i \rightarrow 1$

5) Which of the following statements is/are true? **None. All of them are almost true.**

$\sum_i x_i d\gamma_i = 0$ → γ_i is not a molar property, although $\ln \gamma_i$ is.

$\sum_i x_i \ln \gamma_i = 0$ → should be G^E/RT, not 0.

$\sum_i x_i \frac{d(\ln \gamma_i)}{dx_i} = 0$ → almost like Gibbs-Duhem; but the terms have to be differentiated with respect to one thing (say x_1 or x_2), not to each x_i

$\sum_i x_i \frac{d\gamma_i}{dx_i} = 0$ → combination of the first and third; not correct.

6)

For a binary mixture, the following expression for G is given. What is γ_1?

$$G = x_1 G_1 + x_2 G_2 + RT\, x_1 (A/2\, x_2 + \ln x_1) + RT x_2 (A/2\, x_1 + \ln x_2) \qquad (*)$$

If we want γ_1, we usually get it through G^E expression.

$G^E = G - G^{id}$ (**)

$G^{id} = x_1 G_1 + x_2 G_2 + RT\,(x_1 \ln x_1 + x_2 \ln x_2)$ (***) see Section 11.8 of textbook for derivation

Plugging in (*) and (***) into (**):

$$G^E = RT\, x_1 (\frac{A}{2} x_2) + RT x_2 (\frac{A}{2} x_1) = ARTx_1 x_2 \quad \rightarrow \quad \frac{G^E}{RT} = Ax_1 x_2$$

This form is one of the simplest model for G^E (see p.432 of your textbook). Calculating γ_1:

$$\ln \gamma_1 = \bar{G}_1^E / RT = \left(\frac{\partial (n G^E / RT)}{\partial n_1} \right)_{T,P,n_2} = \left(\frac{\partial (nAx_1 x_2)}{\partial n_1} \right)_{T,P,n_2}$$

$x_1 = n_1/n$ and $x_2 = n_2/n$ where $n = n_1 + n_2$

$$\ln \gamma_i = A \frac{\partial}{\partial n_1} \left(n \frac{n_1 n_2}{n^2} \right)_{T,P,n_2} = A \frac{\partial}{\partial n_1} \left(\frac{n_1 n_2}{n_1 + n_2} \right)_{T,P,n_2} = A \left[\frac{n_2 (n_1 + n_2) - n_1 n_2}{(n_1 + n_2)^2} \right] = A \frac{n_2^2}{(n_1 + n_2)^2} = Ax_2^2$$

$\gamma_1 = \exp(Ax_2^2)$ [and similarly, $\gamma_2 = \exp(Ax_1^2)$]