

Integrating:  $(\bar{H}_2)_{x_1} - (\bar{H}_2)_{x_1^\phi} = - \int_{x_1^\phi}^{x_1} \frac{x_1}{x_2} \left( \frac{\partial \bar{H}_1}{\partial x_1} \right) dx_1$

Let  $x_1^\phi = 0$  (pure 2) then  $(\bar{H}_2)_{x_1^\phi} = \bar{H}_2$

H is obtained from  $H = x_1 \bar{H}_1 + x_2 \bar{H}_2$

### Ideal Gas Mixtures and Fugacities

For a pure component ideal gas, we know

$PV = RT$   $u = u(T)$  only. ig means "ideal gas".

$$G = \mu \quad \left( \frac{\partial G}{\partial P} \right)_T = V = \frac{RT}{P} \Rightarrow \mu^{ig} = \int_{P^\phi}^P \frac{RT}{P} dP + \mu^\phi(T, P^\phi)$$

$$\Rightarrow \boxed{\mu^{ig} = RT \ln P + \lambda(T)}$$

For an ideal gas mixture,  $\boxed{\bar{G}_i^{ig} = \mu_i^{ig} = RT \ln p_i + \lambda_i(T)}$

where  $p_i = y_i P$

Note that both expressions diverge as  $P \rightarrow \phi$ .

Note also that the temperature dependence of the chemical potential has an arbitrary reference constant:

$$\left( \frac{\partial \mu}{\partial T} \right)_P = \left( \frac{\partial G}{\partial T} \right)_P = S \quad (\text{for 1-component})$$

$$\left( \frac{\partial \mu_i}{\partial T} \right)_{P, N} = \left( \frac{\partial \bar{G}_i}{\partial T} \right)_{P, N} = \bar{S}_i \quad (\text{for } n\text{-component})$$

The fugacity is a measure of the chemical potential that does not diverge as  $P \rightarrow 0$  or  $y_i \rightarrow 0$

For a component in a mixture, we define the

$$\text{fugacity } \hat{f}_i \text{ as } \bar{G}_i = \mu_i = RT \ln \hat{f}_i + \lambda_i(T)$$

We use a  $\hat{\phantom{x}}$  to distinguish from the pure component fugacity of  $i$ :  $\hat{f}_i$ , defined as

$$G_i = \mu_i(\text{pure}) = RT \ln \hat{f}_i + \lambda_i(T)$$

Although fugacities have units of pressure, they are really just a measure of the chemical potential.

$$\text{As } P \rightarrow 0, \quad \hat{f} \rightarrow P \quad \hat{f}_i \rightarrow y_i P$$

The difference between the chemical potential in a mixture and an ideal gas mixture is

$$\begin{aligned} \bar{G}_i(T, P, y_i) - \bar{G}_i^{\text{IGM}}(T, P, y_i) &= \mu_i(T, P, y_i) - \mu_i^{\text{IGM}}(T, P, y_i) \\ &= RT \ln \frac{\hat{f}_i}{y_i P} = RT \ln \underbrace{\phi_i}_{\text{fugacity coefficient}} \end{aligned}$$

### Pressure and Temp. Dependence

$$RT \left. \frac{\partial \ln \hat{f}_i}{\partial P} \right|_{T, N} = \left. \frac{\partial \bar{G}_i}{\partial P} \right|_{T, N} = \bar{V}_i$$

For the temperature dependence,  $\left. \frac{\partial \bar{G}}{\partial T} \right|_{P, N} = S$  is not very useful.

$$\text{However, from } \left. \frac{\partial}{\partial T} \left( \frac{G}{T} \right) \right|_{P, N} = \left. \frac{\partial}{\partial T} \left( \frac{H}{T} - S \right) \right|_{P, N} = - \frac{H}{T^2}$$

$$\text{we get } \left. \frac{\partial}{\partial T} \left[ \frac{RT \ln \hat{f}_i}{T} \right] \right|_{P, N} = - \frac{\bar{H}_i - H_i^{\circ}}{T^2} \Rightarrow$$

$$\left. \left( \frac{\partial \ln \hat{f}_i}{\partial T} \right) \right|_{P, N} = - \frac{\bar{H}_i - H_i^{\circ}}{RT^2}$$

$\phi_i$  and  $\hat{f}_i$  can be calculated from a PVT equation of state:

$$RT \ln \phi_i = RT \ln \frac{\hat{f}_i}{y_i P} = \bar{G}_i(T, P, y_i) - \bar{G}_i^{\text{IGM}}(T, P, y_i)$$

$$= - \int_{\infty}^V \left[ \left( \frac{\partial P}{\partial N_i} \right)_{T, V, N_j} - \frac{RT}{V} \right] dV - RT \ln Z$$

$$Z = \frac{PV}{nRT}$$

The proof involves obtaining  $\left( \frac{\partial \bar{G}_i}{\partial V} \right)_{P, N} = \left( \frac{\partial P}{\partial N_i} \right)_{T, N_j}$

and taking into account that the volume of an ideal gas at  $P$  is different than the volume of the real system.

### Ideal (liquid) mixtures and activities

Liquid mixtures are far from ideal gases. However, mixtures of similar components approximate an "ideal" mixture defined from:

$$\bar{G}_i^{\text{ID}}(T, P, x_i) = RT \ln x_i +$$

$$+ \underbrace{G_i(T, P)}_{\text{pure component}}$$

The activity is a measure of the chemical potential as well:

$$RT \ln a_i + G_i(T, P) = \bar{G}_i = \mu_i \Rightarrow$$

$$\Rightarrow RT \ln a_i = \bar{G}_i(T, P, x_i) - \bar{G}_i^{\text{ID}}(T, P, x_i) + RT \ln x_i$$

Activity coefficient:  $\gamma_i = \frac{a_i}{x_i}$

I prefer chemical potentials!

# Mixture Properties (9)

Useful limiting expressions:

For ideal solutions

$$\hat{f}_i = x_i f_i$$

"Lewis -  
Randall  
Rule"

$\nearrow$   
 fugacity in  
 mixture of  
 composition  $x_i$

$\uparrow$   
 pure  
 component  
 fugacity

For dilute solutions, Henry's Law is followed:

$$\hat{f}_i (x_i \rightarrow 0) \rightarrow \underbrace{k_i}_{\text{Henry's "constant", function of temperature + solvent, units of pressure}} x_i = \underbrace{f_i^{**}}_{\text{hypothetical standard state}} x_i$$

Henry's "constant", function of temperature + solvent, units of pressure

hypothetical standard state

Activity coefficients can be normalized with respect to either (a) pure component ( $x_i \rightarrow 1$ ) or (b) infinite dilution ( $x_i \rightarrow 0$ )

In case (a)  $\gamma_i \rightarrow 1$  as  $x_i \rightarrow 1$  ("symmetric" normalization)

(b)  $\gamma_i \rightarrow 1$  as  $x_i \rightarrow 0$  ("asymmetric" normalization)

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Useful limiting expressions:

For ideal solutions

$$\hat{f}_i = x_i f_i$$

$\uparrow$  fugacity in mixture of composition  $x_i$        $\uparrow$  pure component fugacity

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For many real mixtures, "regular solution" behavior is a better approximation than ideal solutions - in that

case,  $\int_0^1 \ln \gamma_j dx_j$  for all components, so that

$$\Delta \underline{S}^{\text{mix}} = \Delta \underline{S}^{\text{ID}} = -R \sum_j N_j \ln \gamma_j$$