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Supplementary References

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Ideal-Gas Mixtures

If n moles of an ideal gas mixture occupy a total volume V^t at temperature T , the pressure is

$$P = \frac{nRT}{V^t}$$

If the n_i moles of species i in this mixture occupy the same total volume alone at the same temperature, the pressure is

$$p_i = \frac{n_i RT}{V^t}$$

Dividing the latter equation by the former one

$$\frac{p_i}{P} = \frac{n_i RT}{V^t} \frac{V^t}{nRT} = \frac{n_i}{n} = x_i$$

$$\text{or } p_i = P x_i \quad (i = 1, 2, \dots, N)$$

Fugacity and Fugacity Coefficient for a Pure Species

As evident from Eq. (1.10) the chemical potential μ_i is fundamental to the formulation of criteria for phase equilibria. This is true as well for chemical reaction equilibria. However, the chemical potential exhibits certain unfortunate characteristics which discourage its use in the solution of practical problems.

The Gibbs energy, and hence μ_i , is defined in relation to the internal energy and entropy, both primitive quantities for which absolute values are unknown. As a result, we have no unequivocal absolute values for the chemical potential.

Moreover, Eq. (1.11) shows that for an ideal gas mixture μ_i approaches negative infinity when either P or x_i approaches zero. This observation is not limited to ideal gases, but is true for any gas.

While these characteristics do not preclude the use of chemical potential, the application of equilibrium criteria is facilitated by introduction of the fugacity, a quantity that takes the place of μ_i but which does not exhibit its less desirable characteristics.

The origin of the fugacity concept resides in Eq. , an equation valid only for pure species i in the ideal-gas state. For a real fluid, we write an analogous equation:

$$G_i \equiv \Gamma_i(T) + RT \ln f_i$$

in which pressure P is replaced by a new property f_i , which has units of pressure. This equation serves as a partial definition of f_i , which is called the fugacity of pure species i .

$$G_i - G_i^{\text{ig}} = RT \ln \frac{f_i}{P} = G_i^{\text{R}} = RT \ln \phi_i$$

According to the definition of Eq. $G_i - G_i^{\text{ig}} = G_i^{\text{R}}$ is the residual Gibbs energy. The dimensionless ratio f_i/P is a new property called the fugacity coefficient and given the symbol ϕ_i . Thus

$$\phi_i \equiv \frac{f_i}{P}$$

We now complete the definition of fugacity by setting the ideal-gas state fugacity of pure species i equal to its pressure:

$$f_i^{\text{ig}} = P$$

Thus for the special case of an ideal gas, $G_i^{\text{R}} = 0$, $\phi_i = 1$, and Eq. $G_i - G_i^{\text{ig}} = RT \ln \frac{f_i}{P}$ is recovered from Eq. $G_i - G_i^{\text{ig}} = RT \ln \phi_i$

Compressed Liquid

(1) Because of the equality of fugacities of saturated liquid and vapour, the calculation of fugacities for species i as a compressed liquid is done in two steps. First, one calculates the fugacity coefficient of saturated vapour $\phi_i^v = \phi_i^{\text{sat}}$ by an integrated form of Eq.

$$f_i^l = f_i^{\text{sat}} = \phi_i^{\text{sat}} P_i^{\text{sat}}$$

(2) The second step is the evaluation of the change in fugacity of the liquid with an increase in pressure above P_i^{sat} .

$$G_i - G_i^{\text{sat}} = \int_{P_i^{\text{sat}}}^P V_i dP$$

Since V_i , the liquid-phase molar volume, is very weak function of P at temperatures well below T_c , an excellent approximation is often obtained when evaluation of the integral is based on the assumption that V_i is constant at the value for saturated liquid, V_i^l :

$$\ln \frac{f_i}{f_i^{\text{sat}}} = \frac{V_i^l (P - P_i^{\text{sat}})}{RT}$$

constant $V_i \approx V_i^l$ ← saturated liquid

Substituting $f_i^{\text{sat}} = \phi_i^{\text{sat}} P_i^{\text{sat}}$ and solving for f_i gives

$$f_i = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \underbrace{\frac{V_i^l (P - P_i^{\text{sat}})}{RT}}_{\text{Pointing factor}}$$

The exponential is known as the Poynting factor (John Henry Poynting (1852-1914), British physicist).

----- Fugacity and Fugacity Coefficient for Species in Solution

The definition of the fugacity of a species in solution is parallel to the definition of the pure-species fugacity. We simply write for species i in a mixture of real gases or in a solution of liquids an equation analogous to the ideal-gas expression, Eq.

$$\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i$$

where \hat{f}_i is the fugacity of species i in solution, replacing the product $x_i P$. Since it is not a partial property, we identify it by a circumflex rather than an overbar.