

Ideal Gases

Properties of ideal gases are relatively easy to calculate, which has been the entire basis of the use of departure functions in Chapter 7. The ideal gas is also a convenient starting point to introduce the calculation of mixture properties and component fugacities. Since ideal gas molecules do not have intermolecular potentials, the internal energy consists of entirely kinetic energy. When components are mixed at constant temperature and pressure, the internal energy is simply the sum of the component internal energies, which can be written

$$\underline{U}^{ig} = \sum_i y_i U_i^{ig} \quad \text{or} \quad \underline{U}^{ig} = \sum_i n_i U_i^{ig} \quad (ig) 0.1$$

The total volume of a mixture is related to the number of moles

$$\underline{V}^{ig} = \left(RT \sum_i n_i \right) / P \quad (ig) 0.2$$

Combing U and V to obtain the definition of H , $H = U + PV$ and using Eqns. 0.1 and 0.2

$$\underline{H}^{ig} = \sum_i n_i U_i^{ig} + RT \sum_i n_i = \sum_i n_i (U_i^{ig} + RT) = \sum_i n_i H_i \quad (ig) 0.3$$

Therefore the enthalpy of a mixture is given by the sum of the enthalpies of the components at the same temperature and pressure. On a molar basis,

$$H^{ig} = \sum_i y_i H_i^{ig} \quad (ig) 0.4$$

Entropy for an ideal gas mixture is more complicated because, as shown in Chapter 3, even systems of fixed total energy have an entropy change associated with mixing due to the distinguishability of the components. The entropy of an ideal gas is calculated by the sum of the entropies of the components plus the entropy change of mixing as given in Chapter 3,

$$\underline{S}^{ig} = \sum_i n_i S_i^{ig} + \Delta S_{mix} = \sum_i n_i S_i^{ig} - R \sum_i n_i \ln y_i \quad \text{or} \quad S^{ig} = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i \quad (ig) 0.5$$

The Gibbs energy and the fugacity will be at the core of phase equilibria calculations. The Gibbs energy of an ideal gas is obtained from the definition, $G \equiv H - TS$. Using H^{ig} and S^{ig} from above,

$$\underline{G}^{ig} \equiv \underline{H}^{ig} - T \underline{S}^{ig} = \sum_i n_i H_i^{ig} - T \left(\sum_i n_i S_i^{ig} - R \sum_i n_i \ln y_i \right) = \sum_i n_i G_i^{ig} + RT \sum_i n_i \ln y_i \quad (ig) 0.6$$

The chemical potential of a component is given by Eqn. 9.6 and taking the derivative of Eqn. 0.6,

$$\mu_i^{ig} = \left(\partial \underline{G}^{ig} / \partial n_i \right)_{T, P, n_{j \neq i}} = G_i^{ig} + RT \left(\partial \left(\sum_i n_i \ln y_i \right) / \partial n_i \right)_{T, P, n_{j \neq i}} \quad (ig) 0.7$$

The derivative is most easily seen by expanding the logarithm before differentiation, $\ln y_i = \ln n_i - \ln n$. Then,

$$\left(\partial \left(\sum_i n_i \ln n_i - \sum_i n_i \ln n \right) / \partial n_i \right)_{T, P, n_{j \neq i}} = \ln n_i + 1 - 1 - \ln n = \ln y_i \quad 0.8$$

therefore

$$\boxed{\mu_i^{ig} = G_i^{ig} + RT \ln y_i} \quad (ig) 0.9$$

By Eqn. 9.14, using Eqn. 0.8 and Eqn. 9.11,

$$\mu_i^{ig} - \mu_{i,pure}^{ig} = RT \ln \frac{f_i^{ig}}{f_{i,pure}^{ig}} = RT \ln y_i \quad \text{or} \quad f_i^{ig} = y_i f_{i,pure}^{ig} \quad (ig) 0.10$$

! The fugacity of a component in an ideal-gas mixture is particularly simple, it is equal to the $y_i P$, the partial pressure!

Since by Eqn. 8.22, $f_{pure}^{ig} = P$,

$$\boxed{f_i^{ig} = y_i P} \quad (ig) 0.11$$

Therefore the fugacity of an ideal gas component is simply its partial pressure. This makes the ideal gas fugacity easy to quantify rapidly. One of the goals of the calculations that will be pursued in Chapter 10 is the quantification of the deviations of the fugacity from ideal gas values quantified by the component fugacity coefficient.