

15.2: The Chemical Potential and Activity of a Gas

To make predictions about processes involving substance A , we need information about the chemical potential of A . Introducing the fugacity does not introduce new information; the fugacity is merely a convenient way to relate the chemical potential to the composition of the system. The fugacity relationship is valid whether we can actually measure μ_A and $\mu_A^o(HIG^o)$ or not. To use the relationship for practical calculations, we must know both, of course.

We introduce the activity function to cope with situations in which we cannot measure the fugacity. For volatile liquids—or solids—we can obtain the Gibbs free energy of formation for both the condensed phase and for the hypothetical ideal-gas standard state. In Section 15.4, we consider the relationship between the two.

The chemical activity of substance A measures the change in the chemical potential when one mole of A in some arbitrarily chosen standard state passes into a very large system of specified composition. We introduce

$$\mu_A = \tilde{\mu}_A^o + RT \ln \left[\frac{\tilde{a}_A}{\tilde{a}_A(ss)} \right]$$

where, as always,

$$\mu_A = \left(\frac{\partial G}{\partial n_A} \right)_{P,T,n_{i \neq A}}$$

We let the activity of A in the arbitrarily chosen standard state, designated “ ss ”, be unity, so that $\tilde{a}_A(ss) = 1$ and the chemical potential of A in this standard state is $\tilde{\mu}_A^o$. The activity, \tilde{a}_A , is a function of the pressure, temperature, and composition of the system.

While we are free to choose any standard state we please for the activity of a gas, the hypothetical ideal-gas standard state is the most practical. In this case, the activity of a gas is given by

$$\tilde{a}_A(P) = \frac{f_A(P)}{f_A(HIG^o)}$$

and

$$\tilde{\mu}_A^o = \mu_A^o(HIG^o)$$

Then the only difference between fugacity and activity is that fugacity has the units of pressure, whereas activity is dimensionless. For any gas in any state, we have

$$\frac{\mu_A - \mu_A^o(HIG^o)}{RT} = \ln \left[\frac{f_A(P)}{f_A(HIG^o)} \right] = \ln[\tilde{a}_A(P)]$$

For an ideal-gas mixture whose pressure is P and in which the mole fraction of A is x_A , we have

$$\tilde{a}_A(x_A, P) = \frac{f_A(x_A, P)}{f_A(HIG^o)} = \frac{x_A P}{P^o}$$

(ideal gas mixture)

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