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The Ideal Solution

The ideal gas is a useful model of the behaviour of gases, and serves as a standard to which real-gas behaviour can be compared. This is formalised by the introduction of residual properties. Another useful model is the ideal solution, which serves as a standard to which real solution behaviour can be compared. We will see in the following section how this is formalised by introduction of excess properties.

Equation ⁱ characterises the behaviour of a constituent species in an ideal-gas mixture:

$$\overline{G}_i^{ig} = G_i^{ig} + RT \ln x_i$$

This equation takes on a new diemension if we replace G_i^{ig}, the Gibbs energy of pure species **i** in the ideal-gas state, by G_i, the Gibbs energy of pure species **i** as it accually exists at the mixture T and P and in the same physical state (real-gas, liquid, or solid) as the mixture. We can then apply it to species in real solutions, indeed to liquids and solids as well as to gases. We therefore define an ideal solution as one for which

$$\overline{G}_i^{id} = G_i + RT \ln x_i$$

where supercript **id** denotes an ideal-solution property.

Gibbs energy of pure species (i), (gas, liquid, solid)

All other thermodynamic properties for an ideal solution follow from this equation. Thus whwn Eq.   is differentiated with respect to temperature at constant pressure and composition and then combined with Eq. other Eq   written for an ideal solution, we get

$$\overline{S}_i^{\,id} = -\left(\frac{\partial \overline{G}_i^{\,id}}{\partial T}\right)_{P,x} = -\left(\frac{\partial G_i}{\partial T}\right)_P - R\ln x_i$$

By Eq. 10.4, $\left(\dfrac{\partial G_i}{\partial T}\right)_P = -S_i$, and this becomes

$$\overline{S}_i^{\,id} = S_i - R \ln x_i$$

Similarly,

$$\overline{V}_i^{\,id} = \left(\frac{\partial \overline{G}_i^{\,id}}{\partial P}\right)_{T,x} = \left(\frac{\partial G_i}{\partial P}\right)_T$$

and

$$\overline{V}_i^{\,id} = V_i$$

Since $\overline{H}_i^{id} = \overline{G}_i^{id} + T\overline{S}_i^{id}$, substitutions by Eqs. 1

$$\overline{H}_i^{id} = G_i + RT \ln x_i + TS_i - RT \ln x_i = G_i + TS_i = H_i$$

or

$$\overline{H}_i^{id} = H_i$$

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The summability relation, applied to the special case of an ideal solution is written

$$M^{id} = \sum_i x_i \overline{M}_i^{id}$$

A

$$G^{id} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i$$

$$S^{id} = \sum_i x_i S_i - R \sum_i x_i \ln x_i$$

$$V^{id} = \sum_i x_i V_i$$

$$H^{id} = \sum_i x_i H_i$$

The Lewis/Randall Rule

The composition dependence of the fugacity of a species in an ideal solution is particularly simple.

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

$$G_i \equiv \Gamma_i(T) + RT \ln f_i \qquad\qquad \text{substraction yields the}$$

general equation

$$\mu_i - G_i \equiv RT\left(\ln \hat{f}_i - \ln f_i\right) \Rightarrow \mu_i = G_i + RT \ln\left(\frac{\hat{f}_i}{f_i}\right)$$

For the special case of an ideal solution

$$\mu_i^{id} = \overline{G}_i^{\,id} = G_i + RT\ln\left(\frac{\hat{f}_i^{\,id}}{f_i}\right)$$

We also found the equation given below

$$\mu_i^{id} = \overline{G}_i^{\,id} = G_i + RT\ln x_i$$ from these two equations

$$\mu_i^{id} = \overline{G}_i^{id} = G_i + RT \ln\left(\frac{\hat{f}_i^{id}}{f_i}\right) = G_i + RT \ln x_i$$

After eliminations, the resulting expression reduces to

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

$$\boxed{\hat{f}_i^{\,id} = x_i f_i}$$

This equation, known as **<u>Lewis/Randall rule</u>**, applies to each species in an ideal solution at all conditions of temperatures, pressure, and composition. It shows that the fugacity of each species in an ideal solution is proportional to its mole fraction; the proportionality constant is the fugacity of pure species i in the same physical state as the solution and at the same T and P.

$$\hat{\phi}_i^{\,id} = \phi_i$$

Thus the fugacity coefficient of species (i) in an ideal solution is equal to the fugacity coefficient of pure species i in the same physical state as the solution and at the same T and P.