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Excess Properties

The residual Gibbs energy and the fugacity coefficient are directly related experimental PVT data

Whereas such data can be adequately correlated by equation of state, thermodynamic property information is advantageously provided by residual properties. Indeed, if convenient treatment of all fluids by means of equations of state were possible, the thermodynamic-property relations already presented would suffice. However, liquid solutionsare often more easily dealt with through properties that measure their deviations, not from ideal-gas behaviour, but from ideal-solution behaviour. Thus the mathematical formalism of excess properties is analogous to that of the resudual properties.

If M represents the molar (a unit-mass) value of any extensive thermodynamic property (e.g., V, U, H, S, G etc), then an excess property M^E is defined as the differnce between the actual property value of a solution and the value it would have as an ideal solution at the same temperature, pressure, and composition. Thus,

$$M^E \equiv M - M^{id}$$

This defination is analogous to the defination of a resudual property However, excess properties have no meaning for pure species, whereas residual properties exist for pure species as well as for mixtures. In addition, we have analogous to Eq.

$$\bar{M}_i^E = \bar{M}_i - \bar{M}_i^{id}$$

where $\bar{M}_i^E$ is a partial excess property. The fundamental excess property relation is derived in exactly the same way as the fundemental residual-property relation and leads to analogous results. written for special case of an ideal solution,

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}dP - \frac{nH^E}{RT^2}dT + \sum_i \frac{\bar{G}_i^E}{RT}dn_i$$

This is the fundemantal excess-property relation, analogous to the fundemantal residual-property relation.

The Excess Gibbs Energy and Activity Coefficient

The excess Gibbs energy is of particular interest. Equation may be written

$$\bar{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i$$

In accord wirh Eq. 10.84 for an ideal solution, this becomes

$$\bar{G}_i^{id} = \Gamma_i(T) + RT \ln x_i \hat{f}_i$$

By difference

$$\bar{G}_i - \bar{G}_i^{id} = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

The difference on the left is the partial excess Gibbs energy $\bar{G}_i^E$; the diemsionless ratio $\hat{f}_i / x_i f_i$ appearing on the right is called the activity coefficient of species i in solution, and is given the symbol γ_i . Thus, by defination,

$$\boxed{\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i}}$$

and

$$\boxed{\bar{G}_i^E = RT \ln \gamma_i}$$

Excess Property Relations

$$\boxed{d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}dP - \frac{nH^E}{RT^2}dT + \sum_i \ln\gamma_i dn_i}$$

Again, the generality these equations precludes their direct practical application. Rather, we make use of restricted forms, which are written by inspection:

$$\frac{V^E}{RT} = \left[\frac{\partial\left(G^E/RT\right)}{\partial P}\right]_{T,x}$$

$$\frac{H^E}{RT} = -T\left[\frac{\partial\left(G^E/RT\right)}{\partial T}\right]_{P,x}$$

and

$$\boxed{\ln\gamma_i = \left[\frac{\partial\left(nG^E/RT\right)}{\partial n_i}\right]_{P,T,x}}$$

The last relation demonstrates that $\ln\gamma_i$ is a partial property with respect to G^E/RT.

$$\left(\frac{\partial\ln\gamma_i}{\partial P}\right)_{T,x} = \frac{\overline{V}_i^E}{RT}$$

and

$$\left(\frac{\partial\ln\gamma_i}{\partial T}\right)_{P,x} = -\frac{\overline{H}_i^E}{RT^2}$$

Since $\ln \gamma_i$ is a partial property with respect to G^E/RT, we may write the following forms of the summability and Gibbs/Duhem equations:

$$\boxed{\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i}$$

and

$$\boxed{\sum_i x_i d \ln \gamma_i = 0} \qquad \text{(const T, P)}$$