

Supplementary Notes for Chapter 9 Mixture Thermodynamics

Key points

Nine major topics of Chapter 9 are reviewed below:

1. Notation and operational equations for mixtures
2. $PVTN$ EOSs for mixtures
3. General effects of mixing on heat and work interactions and state property changes
4. Gibbs-Duhem relationship and thermodynamic consistency
5. Mixing functions
6. Ideal gas mixtures and ideal solutions
7. Fugacity and activity concepts
8. Fugacity coefficients from $PVTN$ EOS property relationships
9. Activity coefficients from ΔG^{EX} property relationships
10. Ideal reversible work effects in mixing or separating components

1. Notation and operational equations for mixtures

Partial molar properties are extensive properties that determine how derived properties change as a function of mole number or composition. For a general property, B , which could be U , H , S , V , or A , the partial molar B is defined as:

$$\bar{B}_i = \left[\frac{\partial B}{\partial N_i} \right]_{T,P,N_j[i]} \quad (9-8)$$

There are a few important relationships in Chapter 9 that allow you to calculate partial molar properties given the extensive form \underline{B} of the property or the intensive form B .

An important one of these is:

$$\bar{B}_i = B - \sum_{j \neq i} x_j \left(\frac{\partial B}{\partial x_j} \right)_{T,P,x[j,i]} \quad (9-53)$$

Note that for a binary, two component system that Eq.(9-53) quickly yields the tangent-intercept method of evaluating partial molar properties from a graph of B versus x_j at constant T and P . For example, see Figure 9.1 and the discussion in the text.

2. $PVTN$ EOSs for mixtures

Volume and pressure explicit equations of state are commonly used to represent the volumetric properties of fluid mixtures of both gases and liquids. The key feature that distinguishes a mixture EOS from its pure component counterpart is the presence of compositional dependence. This dependence expresses itself in the form of so-called “mixing rules” that incorporate pure component EOS parameters and weight them

proportionally to the concentration of each component following a specific mathematical recipe. With the exception of the virial equation of state no rigorous theoretical approach exists to specify a mixing rule recipe. The most common approach is to use some variation of the Lorentz-Bertlelot rules used by van der Waals and others over a century ago (see Eqs (9-17 and 9-18). In mixtures that exhibit considerable non-ideality, a binary or higher order interaction parameter δ_{ij} is introduced to capture specific interactions between molecules of type i and j .

Each mixture $PVTN_i$ EOS will have some prescribed recipe for its mixing rules. For example see the conventions followed for the RK and PR EOS on pages 324- 326. In situations where high level non-ideal effects are present often more complex forms for mixing rules are introduced. The Wong-Sandler and Chueh-Prausnitz rules discussed on pages 327-328 are examples of this type of mixing rule.

3. General effects of mixing on heat and work interactions and state property changes

There are a few typical classes of problems that you should be able to solve. These include:

- Calculating the change in enthalpy as a result of mixing to determine a heat interaction for maintaining a constant temperature or to follow some prescribed recipe for temperature, for example, see Problem 9.2.
- Calculating a change in volume as a result of mixing to determine a change in density or the magnitude of a work interaction at constant pressure.

4. Gibbs-Duhem relationship and thermodynamic consistency

For mixture data and correlations – for any property B , the partial molar quantities are interrelated through the use of the general Gibbs-Duhem relationship:

$$\sum_{i=1}^n x_i d\bar{B}_i = \left[\frac{\partial B}{\partial T} \right]_{P, x_i} dT + \left[\frac{\partial B}{\partial P} \right]_{T, x_i} dP$$

Note that B is a function of T , P , and x_i for $i = 1, \dots, n$. The Gibbs-Duhem relationship can be applied to any partial molar property, such as:

$$\bar{H}_i, \bar{V}_i, \mu_i, \ln \hat{\phi}_i, \ln \hat{f}_i, \bar{G}_i, \ln a_i, \ln \gamma_i, \text{ etc.}$$

For a binary system, the Gibbs-Duhem relationship is frequently used to check thermodynamic consistency of thermodynamic data; for example, activity coefficients. Additionally, for a binary mixture, if you have a measurement of the partial molar property of one component as a function of composition you can determine the property for the other component.

5. Mixing functions

$$\Delta B_{mix} \equiv B(T, P, x_i, i = 1, \dots, n) - \sum_{i=1}^n x_i \bar{B}_i^+(T^+, P^+, x_i^+, i = 1, \dots, n) \quad (9-68)$$

which is in intensive form. A similar expression results for $\Delta \underline{B}_{mix}$ in extensive form with x_i replaced by N_i . You should be familiar with the concept of a reference state (+). Strictly speaking, reference states are arbitrary, but in practice several common forms appear for x_i^+ , T^+ , and P^+ , for example:

- (1) pure i at T and P of the mixture
- (2) $x_i^+ \rightarrow 0$ at T and P of the mixture— that is in an infinite dilution state where Henry's law behavior is followed
- (3) a fixed composition of 1 molal or 1 molar concentration at T and P of the mixture that behaves in some ideal manner – commonly used for electrolytes (see Chapter 12)

6. Ideal gas mixtures and ideal solutions

In this section of the text, a set of definitions were used to characterize non-ideal solutions in terms of a deviation from ideal behavior.

- ideal gas mixture: $\bar{G}_i = \mu_i^{ig} = RT \ln y_i P + \lambda_i(T)$
- ideal solution: $\bar{G}_i = \mu_i^{ID} = RT \ln x_i + \Lambda_i(T, P)$

where λ_i and Λ_i are constants specific to component i . The key points to remember are that partial pressure $y_i P$ is the ideal gas mixture compositionally dependent variable while for ideal condensed phase solution it is the mole fraction x_i .

7. Fugacity and activity concepts

For a real mixture or solution we introduce the following models:

$$\text{real fluid mixture: } \bar{G}_i = \mu_i = RT \ln \hat{f}_i + \lambda_i$$

$$\text{real solution: } \bar{G}_i = \mu_i = RT \ln a_i + \mu_i^+(T^+, P^+, x_i^+)$$

which lead to the following definitions of the fugacity coefficient and activity coefficient $\hat{\phi}_i$ and γ_i , respectively:

$$\hat{\phi}_i \equiv \frac{\hat{f}_i}{y_i P} \quad \text{---- represents a deviation from ideal gas/fluid mixture behavior}$$

and

$$\gamma_i \equiv \frac{\hat{f}_i}{a_i} = \frac{\hat{f}_i}{\hat{f}_i^+ x_i} \quad \text{---- represents a deviation from ideal solution behavior}$$

8. Fugacity coefficient relationships from $PVTN$ EOS property models

There are two basic approaches— one involving pressure explicit EOSs like the PR or RKS, and the other for volume explicit EOSs, such as Virial or Corresponding States formulations, including compressibility expansions in density or molar volume or similarly structured equations. Equations (9-142) and (9-143) provide convenient forms for pressure explicit EOS models for mixture and pure components, respectively, while Eqs(9-129) and (9-127) work for volume explicit EOS models.

For example, for component i in a mixture:

$$RT \ln \hat{\phi}_i = - \int_{\infty}^V \left[\left[\frac{\partial P}{\partial N_i} \right]_{T,V,N_j[i]} - \frac{RT}{V} \right] dV - RT \ln Z$$

or

$$RT \ln \hat{\phi}_i = + \int_0^P \left[\bar{V}_i - \frac{RT}{P} \right] dP$$

At this point you should know how to calculate the fugacity or fugacity coefficient for a pure component using a pressure- or volume-explicit EOS or for a component in a binary mixture using a suitable $PVTN$ EOS that has been properly formulated with mixing rules for its constants (for example, the a_{mix} and b_{mix} constants in the RKS EOS) in terms of pure component properties and a binary interaction parameter, eg δ_{ij} . Being able to do this provides a powerful tool for calculations required later in the course, for example to estimate the vapor pressure of a pure component you would equate $\hat{\phi}_i$ for the liquid and vapor phases at a given temperature by estimating the P and using the EOS to calculate liquid and vapor volumes (densities) until the fugacity coefficients for each phase were equal.

9. Activity coefficients from ΔG^{EX} property relationships

The activity coefficient is defined in terms of the partial molar excess Gibbs free energy of mixing and can be directly related to the fugacity using the definition of activity:

$$RT \ln \gamma_i = \bar{\Delta G}_i^{EX} = \left(\frac{\partial \Delta \underline{G}^{EX}}{\partial N_i} \right)_{T,P,N_j[i]}$$

$$\text{where } \gamma_i \equiv a_i / x_i = \hat{f} / \hat{f}_i^+ x_i$$

To evaluate the partial derivative we need an expression for $\Delta \underline{G}^{EX}$:

$$\Delta \underline{G}^{EX} \equiv \Delta \underline{G}_{mix} - \Delta \underline{G}^{ID} = f [T, P, N_i (i=1, \dots, n)]$$

which represents the difference between the actual enthalpy of mixing and the enthalpy of mixing for an ideal solution at the same T , P and composition as the actual mixture.

Typically, one has access to a model that gives $\Delta G^{EX} = \Delta \underline{G}^{EX} / N$ as a function of T , P , and x_i , and with Eq. (9-53) one can easily obtain γ_i for each component, e.g.

$$RT \ln \gamma_i = \Delta G^{EX} - \sum_{j \neq i} x_j \left(\frac{\partial \Delta G^{EX}}{\partial x_i} \right)_{T,P,x[j,i]}$$

In addition, the Gibbs-Duhem equation can be applied to calculate the other activity coefficient given a set of data for one component (e.g. if γ_{solvent} is known as a function of composition then γ_{solute} can be estimated by integrating the Gibbs-Duhem relationship). Conversely, if both activity coefficients of a binary mixture are known then the Gibbs-Duhem equation can be used to check the thermodynamic consistency of a given set of data. For example, the slope and area tests have been developed specifically for this purpose (see pages 357-358 and Fig. 9.3).

A key issue here is how to deal with the standard or reference state condition (+), as that will have a direct effect on the magnitude and behavior of γ_i . If a symmetric reference state is used then $\hat{f}_i^+ = f_i(\text{pure } i)$ and the Lewis and Randall rule is followed as x_i goes to 1.0 with γ_i approaching 1.0. Alternatively, a unsymmetrical reference state can be used where the infinite dilution behavior as defined by Henry's Law determines that γ_i^{**} approaches 1.0 as x_i goes to 0. This is frequently called the McMillan-Mayer reference condition. Another popular alternative commonly employed for electrolytes is to use a 1 molal solution at T and P of the mixture where the mixture follows Henry's Law in dilute solutions as x_i or $m_i \rightarrow 0$ (see Fig. 9.9 for example).

The discussion in the text from pages 360 to 365 should be carefully reviewed to see how the activity coefficient is related to fugacity behavior for different reference state conditions. Particular attention should be paid to Figures 9.6 – 9.9.

10. Ideal reversible work associated with mixing or separating components

Under isothermal conditions the reversible work is equal to the net change in Gibbs free energy associated with the process, more generally the reversible work can be related directly to the change in availability using the methods introduced in Chapter 14. Examples 9.8 and 9.9 should be reviewed to see how the concepts are employed. The approach is quite straightforward if you are dealing with a steady state process. Things are a bit more complicated if the system or process conditions are changing with time, but the general concept remains unchanged.