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An algebraic formulation for an equal area rule to determine phase compositions in simple reactive systems

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Abstract

Equal area rules are fundamental constructs in thermodynamics for determining conditions of equilibrium. The Maxwell equal area rule (MEAR) provides saturated volumes when the two-phase isotherm/isobar cuts the van der Waals loops such that the areas above and below are equal. Another equal area rule exists for determining the phase compositions in a binary mixture when plotting the derivative of the total Gibbs energy against the composition. In this work, we show that in the determination of phase compositions in reactive systems, an equal area rule exists under the correct transformation of the mole fractions.

Keywords: Chemical equilibrium; Phase equilibrium; Equal areas; Compositions; Reactive systems

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John M. Prausnitz

One of us (KRH) had the singular good fortune to have John as his instructor in graduate thermodynamics at Berkeley and to have benefited form some discussions with him. At that time, I had not really settled upon a research area in which I was passionate, but John changed that and instilled an excitement in me for the field that has lasted 43 years. Although for personal reasons, I could not remain at Berkeley and study under his tutelage, I have always felt that John was available for consultation and advice throughout my career. I have benefited enormously from this relationship, and I am certain that everyone has who has come into contact with this exceptional person feels the same.

From John, I learned to think differently from the crowd. I would like to think that he enjoys reading this paper that extends a common thermodynamics construct to chemical equilibrium. Even an experimentalist dabbles in theory sometimes.

1. Introduction

Two equal area rules have appeared in the literature for determining equilibrium conditions. The classical one is the Maxwell equal area rule (MEAR). This construct appears in most thermodynamics textbooks. It locates the equilibrium volumes for pure components from an equation of state (EOS) by equalizing the areas formed by the van der Waals loops of an isotherm.

More recently, Eubank and Hall [1] proved the existence of another equal area rule that enabled finding the equilibrium compositions for binary mixtures at constant temperature and pressure. They plotted the mole fraction derivative of the total Gibbs energy against composition to find the equilibrium compositions using an equal area rule. Shyu et al. [2] used the equal area method to calculate the compositions of two or three phases in equilibrium for ternary systems. Hanif et al. [3,5] discussed MEAR in connection with pure component phase equilibrium using an EOS. Then, Shyu et al. [4] proposed the maximum partial area rule for applying the equal area rule to phase equilibrium calculations. Later, Hanif et al. [3,5] extended the use of the equal area rule for calculating multi-phase equilibrium problems. Finally, Iglesias-Silva et al. [6] collected all the equal area techniques into an efficient algebraic method. Recently, Ung and Doherty [7,8] used transformed mole fractions to solve the problem of phase equilibrium in reactive systems. Using this transform changed the constrained problem into an unconstrained problem.

In this work, we have used the transformed mole fractions and show that an equal area construct can determine the phase

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compositions in simple reactive systems. The numerical procedure using equal area to determine the composition in reactive systems is simple and fast.

2. Derivations

The total Gibbs energy of a C-component, R-reaction mixture is:

$$G = \sum_{i=1}^{C} n_i \mu_i \tag{1}$$

subject to R equilibrium reactions:

$$\sum_{i=1}^{C} \nu_{i,j}\mu_i = 0 \quad \text{for} \quad j = 1, 2, \ldots, R \tag{2}$$

where n_i is the number of moles of component i, μ_i is the chemical potential of component i and $\nu_{i,j}$ is the stoichiometric coefficient of component i in reaction j. This means that only $(C-R)$ mole fractions are independent variables. Ung and Doherty [7,8] transform the mole fraction using R reference components to achieve an unconstrained system of $(C-R)$ equations. They use:

$$X_i = \frac{\hat{n}_i}{\hat{n}_T} = \frac{\left[n_i - \nu_i^T (V_{\text{ref}})^{-1} n_{\text{ref}}\right]}{\left[n_T - \nu_T^T (V_{\text{ref}})^{-1} n_{\text{ref}}\right]} = \frac{\left[x_i - \nu_i^T (V_{\text{ref}})^{-1} x_{\text{ref}}\right]}{\left[1 - \nu_T^T (V_{\text{ref}})^{-1} x_{\text{ref}}\right]} \quad \text{for} \quad i = 1, 2, \ldots, C-R \tag{3}$$

with

$$\nu_i^T = (\nu_{i,1}, \nu_{i,2}, \ldots, \nu_{i,R}) \tag{4}$$

$$\nu_T^T = (\nu_{T,1}, \nu_{T,2}, \ldots, \nu_{T,R}), \quad \nu_{T,i} = \sum_{k=1}^{C} \nu_{k,i} \tag{5}$$

$$n_{\text{ref}} = (n_{C-R+1}, n_{C-R+2}, \ldots, n_C)^T \tag{6}$$

$$x_{\text{ref}} = (x_{C-R+1}, x_{C-R+2}, \ldots, x_C)^T \tag{7}$$

$$\sum_{i=1}^{C-R} X_i = 1 \tag{8}$$

and

$$V_{\text{ref}} = \begin{pmatrix} \nu_{C-R+1,1} & \nu_{C-R+1,2} & \cdots & \nu_{C-R+1,R} \\ \nu_{C-R+2,1} & \nu_{C-R+2,2} & \cdots & \nu_{C-R+2,R} \\ \vdots & \vdots & \ddots & \vdots \\ \nu_{C,1} & \nu_{C,2} & \cdots & \nu_{C,R} \end{pmatrix} \tag{9}$$

in which n_T denotes the total number of moles, x_i is the mole fraction of component i, and n_{ref} and x_{ref} are row vectors of dimension R denoting number of moles and mole fractions of the R reference components, respectively. Eq. (3) depends upon the equilibrium constants for each reaction. Using Eqs. (3)–(9), the Gibbs energy without constraints becomes:

$$G = G(T, P, \hat{n}_1, \hat{n}_2, \ldots, \hat{n}_{C-R}) \tag{10}$$

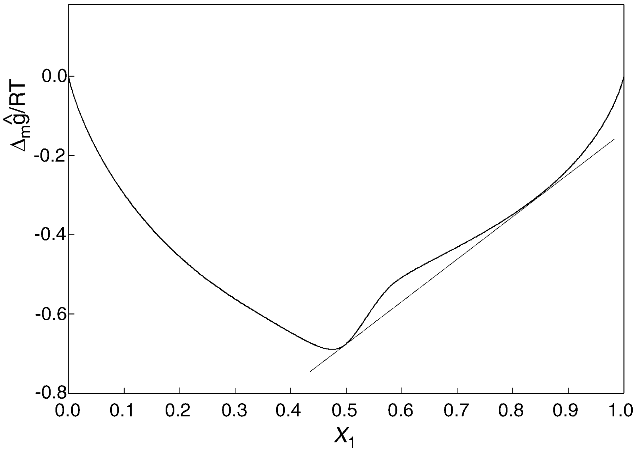

Fig. 1. $(\Delta_m \hat{g}/RT)$–X_1 plot showing similar behavior as an unconstrained Gibbs energy of mixing.

The unconstrained, transformed molar Gibbs energy is:

$$\hat{g} = \frac{G}{\hat{n}_T} = \frac{G/n_T}{\left[1 - \nu_T^T (V_{\text{ref}})^{-1} x_{\text{ref}}\right]} = \frac{g}{\left[1 - \nu_T^T (V_{\text{ref}})^{-1} x_{\text{ref}}\right]} \tag{11}$$

where g is the molar Gibbs energy. Then, we can apply normal thermodynamics relationships to Eq. (10) For a binary system in the transformed mole fractions $(C-R=2)$, we can use:

$$\hat{g} = X_1\hat{\mu}_1 + X_2\hat{\mu}_2 \quad \text{with} \quad \hat{\mu}_i = \left(\frac{\partial \hat{n}_T \hat{g}}{\partial \hat{n}_i}\right)_{T,P,\hat{n}_{j=i}} \tag{12}$$

to determine the phase compositions at constant pressure and temperature. The total differential of the transformed Gibbs energy at constant pressure and temperature is:

$$\mathrm{d}\hat{g} = \hat{\mu}_1\,\mathrm{d}X_1 + \hat{\mu}_2\,\mathrm{d}X_2 \tag{13}$$

and the derivative with respect X_1 is:

$$\left(\frac{\partial \hat{g}}{\partial X_1}\right)_{T,P} = \hat{\mu}_1 + \hat{\mu}_2 \frac{\mathrm{d}X_2}{\mathrm{d}X_1} = \hat{\mu}_1 - \hat{\mu}_2 \tag{14}$$

then

$$X_1\left(\frac{\partial \hat{g}}{\partial X_1}\right)_{T,P} = X_1\hat{\mu}_1 - X_1\hat{\mu}_2 = X_1\hat{\mu}_1 - (1 - X_2)\hat{\mu}_2 = X_1\hat{\mu}_1 + X_2\hat{\mu}_2 - \hat{\mu}_2 = \hat{g} - \hat{\mu}_2 \tag{15}$$

At equilibrium, the transformed chemical potential is equal in each phase, therefore:

$$\hat{g}^\alpha - X_1^\alpha \left(\frac{\partial \hat{g}}{\partial X_1}\right)_{T,P}^{\alpha} = \hat{g}^\beta - X_1^\beta \left(\frac{\partial \hat{g}}{\partial X_1}\right)_{T,P}^{\beta} \tag{16}$$

but from Eq. (14), the orthogonal derivative is equal in each phase at equilibrium indicating that a tangent line exists that touches the curve $\hat{g}$ versus X_1 at X_1^α and X_1^β, as shown in Fig. 1. Then Eq. (16) becomes:

$$\hat{g}^\alpha - \hat{g}^\beta - \left(\frac{\partial \hat{g}}{\partial X_1}\right)_{T,P}^{\alpha} (X_1^\alpha - X_1^\beta) = 0 \tag{17}$$