Isothermobaric Ternary Phase Diagrams

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It is always useful to view the thermodynamic phase diagram as a sanity check on kinetic simulations. This is commonly done for binary alloy systems. The process for generating a correct ternary phase diagram is less routine; this document summarizes the derivation from the system free energy functional as a constrained minimization problem.

An exposition of the method is given in part on math.stackexchange.com. The Python source code in this repository provides a complete implementation.

Binary Two-Phase

Consider a binary system with two phases, the free energies of which are defined by the functions $G_\alpha(x)$ and $G_\beta(x)$. The system will have volume fraction v_α of phase α and v_β of phase β. We seek to determine the equilibrium phase compositions (x_α, x_β) and volume fractions that minimize the free energy of the total system, subject to two constraints. To do so, we'll make use of Lagrange multipliers.

$$G(x_\alpha, x_\beta) = v_\alpha G_\alpha(x_\alpha) + v_\beta G_\beta(x_\beta) \tag{1}$$

$$v_\alpha x_\alpha + v_\beta x_\beta = x \tag{2}$$

$$v_\alpha + v_\beta = 1 \tag{3}$$

where x is the system composition. The system functional and integrand are

$$\mathcal{L}[x_\alpha, x_\beta, v_\alpha, v_\beta, \lambda_1, \lambda_2] = \int_V F \mathrm{d}V \tag{4}$$

$$F(x_\alpha, x_\beta, v_\alpha, v_\beta, \lambda_1, \lambda_2) = v_\alpha G_\alpha(x_\alpha) + v_\beta G_\beta(x_\beta) - \lambda_1(v_\alpha x_\alpha + v_\beta x_\beta - x) - \lambda_2(v_\alpha + v_\beta - 1). \tag{5}$$

Therefore, the system of Euler-Lagrange Equations is

$$\frac{\delta\mathcal{L}}{\delta x_\alpha} = \frac{\partial F}{\partial x_\alpha} = 0 = v_\alpha \frac{\partial G_\alpha}{\partial x_\alpha} - \lambda_1 v_\alpha \tag{6}$$

$$\frac{\delta\mathcal{L}}{\delta x_\beta} = \frac{\partial F}{\partial x_\beta} = 0 = v_\beta \frac{\partial G_\beta}{\partial x_\beta} - \lambda_1 v_\beta \tag{7}$$

$$\frac{\delta\mathcal{L}}{\delta v_\alpha} = \frac{\partial F}{\partial v_\alpha} = 0 = G_\alpha(x_\alpha) - \lambda_1 x_\alpha - \lambda_2 \tag{8}$$

$$\frac{\delta\mathcal{L}}{\delta v_\beta} = \frac{\partial F}{\partial v_\beta} = 0 = G_\beta(x_\beta) - \lambda_1 x_\beta - \lambda_2 \tag{9}$$

Solving Eqns. 6 & 7 for λ_1 gives

$$\lambda_1 = \frac{\partial G_\alpha}{\partial x_\alpha} = \frac{\partial G_\beta}{\partial x_\beta} \tag{10}$$

$$\therefore \frac{\partial G_\alpha}{\partial x_\alpha} = \frac{\partial G_\beta}{\partial x_\beta}. \tag{11}$$

Solving Eqns. 8 & 9 for λ_2 and substituting Eqn. 11 gives

$$\lambda_2 = G_\alpha(x_\alpha) - \frac{\partial G_\alpha}{\partial x_\alpha} x_\alpha = G_\beta(x_\beta) - \frac{\partial G_\alpha}{\partial x_\alpha} x_\beta \tag{12}$$

$$\therefore G_\beta(x_\beta) = G_\alpha(x_\alpha) - \frac{\partial G_\alpha}{\partial x_\alpha} \left(x_\alpha - x_\beta\right). \tag{13}$$

Eqn. 11 represents equality of chemical potential, while Eqn. 13 represents equality of grand potential energy. This pair of equations can be solved to determine the two unknown compositions needed to specify the common tangent line containing points $G_\alpha(x_\alpha)$, $G(x)$, and $G_\beta(x_\beta)$.

Ternary Two-Phase

Consider a ternary system with two phases, the free energies of which are defined by the functions $G_\alpha(x_1, x_2)$ and $G_\beta(x_1, x_2)$. The system will have volume fraction v_α of phase α and v_β of phase β. We seek to determine the equilibrium phase compositions $(x_1^\alpha, x_2^\alpha, x_1^\beta, x_2^\beta)$ and volume fractions that minimize the free energy of the total system, subject to three constraints. Unlike the binary case, we must make use of the constraints directly by including Euler-Lagrange equations with respect to the Lagrange multipliers. This is because the common tangent *line* between the two points does not completely specify the equilibrium tangent *plane*.

$$G(x_1^\alpha, x_2^\alpha, x_1^\beta, x_2^\beta) = v_\alpha G_\alpha(x_1^\alpha, x_2^\alpha) + v_\beta G_\beta(x_1^\beta, x_2^\beta) \tag{14}$$

$$v_\alpha x_1^\alpha + v_\beta x_1^\beta = x_1 \tag{15}$$

$$v_\alpha x_2^\alpha + v_\beta x_2^\beta = x_2 \tag{16}$$

$$v_\alpha + v_\beta = 1 \tag{17}$$

where A and B label phases, 1 and 2 label components, x_1 and x_2 are the system compositions, and compositions with labels x_i^j represent the composition of component i in phase j. The integrand is

$$\begin{aligned} F(x_1^\alpha, x_2^\alpha, x_1^\beta, x_2^\beta) = {} & v_\alpha G_\alpha(x_1^\alpha, x_2^\alpha) + v_\beta G_\beta(x_1^\beta, x_2^\beta) \\ & - \lambda_1(v_\alpha x_1^\alpha + v_\beta x_1^\beta - x_1) \\ & - \lambda_2(v_\alpha x_2^\alpha + v_\beta x_2^\beta - x_2) \\ & - \lambda_3(v_\alpha + v_\beta - 1) \end{aligned} \tag{18}$$

The system of Euler-Lagrange Equations becomes

$$\frac{\partial F}{\partial x_1^\alpha} = 0 = v_\alpha \frac{\partial G_\alpha}{\partial x_1^\alpha} - \lambda_1 v_\alpha \tag{19}$$

$$\frac{\partial F}{\partial x_1^\beta} = 0 = v_\beta \frac{\partial G_\beta}{\partial x_1^\beta} - \lambda_1 v_\beta \tag{20}$$

$$\frac{\partial F}{\partial x_2^\alpha} = 0 = v_\alpha \frac{\partial G_\alpha}{\partial x_2^\alpha} - \lambda_2 v_\alpha \tag{21}$$

$$\frac{\partial F}{\partial x_2^\beta} = 0 = v_\beta \frac{\partial G_\beta}{\partial x_2^\beta} - \lambda_2 v_\beta \tag{22}$$

$$\frac{\partial F}{\partial v_\alpha} = 0 = G_\alpha - \lambda_1 x_1^\alpha - \lambda_2 x_2^\alpha - \lambda_3 \tag{23}$$

$$\frac{\partial F}{\partial v_\beta} = 0 = G_\beta - \lambda_1 x_1^\beta - \lambda_2 x_2^\beta - \lambda_3 \tag{24}$$

$$\frac{\partial F}{\partial \lambda_1} = 0 = v_\alpha x_1^\alpha + v_\beta x_1^\beta - x_1 \tag{25}$$

$$\frac{\partial F}{\partial \lambda_2} = 0 = v_\alpha x_2^\alpha + v_\beta x_2^\beta - x_2 \tag{26}$$

$$\frac{\partial F}{\partial \lambda_3} = 0 = v_\alpha + v_\beta - 1 \tag{27}$$

Solving Eqns. 19 & 20 for λ_1 gives

$$\lambda_1 = \frac{\partial G_\alpha}{\partial x_1^\alpha} = \frac{\partial G_\beta}{\partial x_1^\beta} \tag{28}$$

$$\therefore \frac{\partial G_\alpha}{\partial x_1^\alpha} = \frac{\partial G_\beta}{\partial x_1^\beta} \tag{29}$$

This represents equality of chemical potential of component 1. Likewise, solving Eqns. 21 & 22 for λ_2 gives

$$\lambda_2 = \frac{\partial G_\alpha}{\partial x_2^\alpha} = \frac{\partial G_\beta}{\partial x_2^\beta} \tag{30}$$

$$\therefore \frac{\partial G_\alpha}{\partial x_2^\alpha} = \frac{\partial G_\beta}{\partial x_2^\beta} \tag{31}$$

This represents equality of chemical potential of component 2. Solving Eqns. 23 & 24 for λ_3, after substituting Eqns. 29 & 31, gives

$$\begin{aligned}\lambda_3 &= G_\alpha - \frac{\partial G_\alpha}{\partial x_1^\alpha} x_1^\alpha - \frac{\partial G_\alpha}{\partial x_2^\alpha} x_2^\alpha \\ &= G_\beta - \frac{\partial G_\alpha}{\partial x_1^\alpha} x_1^\beta - \frac{\partial G_\alpha}{\partial x_2^\alpha} x_2^\beta \qquad (32)\end{aligned}$$

$$\therefore G_\beta = G_\alpha - \frac{\partial G_\alpha}{\partial x_1^\alpha}(x_1^\alpha - x_1^\beta) - \frac{\partial G_\alpha}{\partial x_2^\alpha}(x_2^\alpha - x_2^\beta). \tag{33}$$

This represents equality of the grand potential of phases A and B.

Substituting Eqn. 27 into Eqns. 25 & 26 gives

$$x_1 = v_\alpha x_1^\alpha + (1 - v_\alpha) x_1^\beta \tag{34}$$

$$x_2 = v_\alpha x_2^\alpha + (1 - v_\alpha) x_2^\beta \tag{35}$$

Solving for v_α gives us the ternary Lever Rule:

$$\begin{aligned}v_\alpha &= \frac{x_1 - x_1^\beta}{x_1^\alpha - x_1^\beta} \\ &= \frac{x_2 - x_2^\beta}{x_2^\alpha - x_2^\beta} \qquad (36)\end{aligned}$$

$$\therefore \frac{x_1 - x_1^\beta}{x_1^\alpha - x_1^\beta} = \frac{x_2 - x_2^\beta}{x_2^\alpha - x_2^\beta}. \tag{37}$$

The system of Eqns. 29, 31, 33 & 37 can be solved to determine the two unknown composition pairs needed to specify the equilibrium tie line containing the points $G_\alpha(x_1^\alpha, x_2^\alpha)$, $G(x_1, x_2)$, and $G_\beta(x_1^\beta, x_2^\beta)$.

Ternary Three-Phase

Consider a ternary system with three phases, the free energies of which are defined by the functions $G_\alpha(x_1, x_2)$, $G_\beta(x_1, x_2)$, and $G_\gamma(x_1, x_2)$. The system will have volume fraction v_α of phase α, v_β of phase β, and v_γ of phase γ. We seek to determine the equilibrium phase compositions $(x_1^\alpha, x_2^\alpha, x_1^\beta, x_2^\beta, x_1^\gamma, x_2^\gamma)$ and volume fractions that minimize the free energy of the total system, subject to three constraints. Like the binary case, we do not make use of the constraints directly because three points completely specify the common tangent *plane*.

$$G(x_1^\alpha, x_1^\beta, x_1^\gamma, x_2^\alpha, x_2^\beta, x_2^\gamma) = v_\alpha G_\alpha(x_1^\alpha, x_2^\alpha) + v_\beta G_\beta(x_1^\beta, x_2^\beta) + v_\gamma G_\gamma(x_1^\gamma, x_2^\gamma) \tag{38}$$

$$v_\alpha x_1^\alpha + v_\beta x_1^\beta + v_\gamma x_1^\gamma = x_1 \tag{39}$$

$$v_\alpha x_2^\alpha + v_\beta x_2^\beta + v_\gamma x_2^\gamma = x_2 \tag{40}$$

$$v_\alpha + v_\beta + v_\gamma = 1 \tag{41}$$

where x_1 and x_2 are the system compositions. The integrand is

$$\begin{aligned} F(x_1^\alpha, x_1^\beta, x_1^\gamma, x_2^\alpha, x_2^\beta, x_2^\gamma) = {} & v_\alpha G_\alpha(x_1^\alpha, x_2^\alpha) + v_\beta G_\beta(x_1^\beta, x_2^\beta) + v_\beta G_\gamma(x_1^\gamma, x_2^\gamma) \\ & - \lambda_1(v_\alpha x_1^\alpha + v_\beta x_1^\beta + v_\gamma x_1^\gamma - x_1) \\ & - \lambda_2(v_\alpha x_2^\alpha + v_\beta x_2^\beta + v_\gamma x_2^\gamma - x_2) \\ & - \lambda_3(v_\alpha + v_\beta + v_\gamma - 1) \end{aligned} \tag{42}$$

The system of Euler-Lagrange Equations becomes

$$\frac{\partial F}{\partial x_1^\alpha} = 0 = v_\alpha \frac{\partial G_\alpha}{\partial x_1^\alpha} - \lambda_1 v_\alpha \tag{43}$$

$$\frac{\partial F}{\partial x_1^\beta} = 0 = v_\beta \frac{\partial G_\beta}{\partial x_1^\beta} - \lambda_1 v_\beta \tag{44}$$

$$\frac{\partial F}{\partial x_1^\gamma} = 0 = v_\gamma \frac{\partial G_\gamma}{\partial x_1^\gamma} - \lambda_1 v_\gamma \tag{45}$$

$$\frac{\partial F}{\partial x_2^\alpha} = 0 = v_\alpha \frac{\partial G_\alpha}{\partial x_2^\alpha} - \lambda_2 v_\alpha \tag{46}$$

$$\frac{\partial F}{\partial x_2^\beta} = 0 = v_\beta \frac{\partial G_\beta}{\partial x_2^\beta} - \lambda_2 v_\beta \tag{47}$$

$$\frac{\partial F}{\partial x_2^\gamma} = 0 = v_\gamma \frac{\partial G_\gamma}{\partial x_2^\gamma} - \lambda_2 v_\gamma \tag{48}$$

$$\frac{\partial F}{\partial v_\alpha} = 0 = G_\alpha - \lambda_1 x_1^\alpha - \lambda_2 x_2^\alpha - \lambda_3 \tag{49}$$

$$\frac{\partial F}{\partial v_\beta} = 0 = G_\beta - \lambda_1 x_1^\beta - \lambda_2 x_2^\beta - \lambda_3 \tag{50}$$

$$\frac{\partial F}{\partial v_\gamma} = 0 = G_\gamma - \lambda_1 x_1^\gamma - \lambda_2 x_2^\gamma - \lambda_3 \tag{51}$$

Solving Eqns. 43, 44 & 45 for λ_1 gives

$$\lambda_1 = \frac{\partial G_\alpha}{\partial x_1^\alpha} = \frac{\partial G_\beta}{\partial x_1^\beta} = \frac{\partial G_\gamma}{\partial x_1^\gamma} \tag{52}$$

$$\therefore \frac{\partial G_\alpha}{\partial x_1^\alpha} = \frac{\partial G_\beta}{\partial x_1^\beta} \tag{53}$$

$$\frac{\partial G_\alpha}{\partial x_1^\alpha} = \frac{\partial G_\gamma}{\partial x_1^\gamma} \tag{54}$$

Eqns. 53 & 54 represent equality of chemical potential of component 1 in pairs of phases $\alpha - \beta$ and $\alpha - \gamma$. Similarly, solving Eqns. 46, 47, & 48 for λ_2 gives

$$\lambda_2 = \frac{\partial G_\alpha}{\partial x_2^\alpha} = \frac{\partial G_\beta}{\partial x_2^\beta} = \frac{\partial G_\gamma}{\partial x_2^\gamma} \tag{55}$$

$$\therefore \frac{\partial G_\alpha}{\partial x_2^\alpha} = \frac{\partial G_\beta}{\partial x_2^\beta} \tag{56}$$

$$\frac{\partial G_\alpha}{\partial x_2^\alpha} = \frac{\partial G_\gamma}{\partial x_2^\gamma} \tag{57}$$

Eqns. 56 & 57 represent equality of chemical potential of component 2 in pairs of phases $\alpha - \beta$ and $\alpha - \gamma$. Solving Eqns. 49, 50 & 51 for λ_3 gives

$$\lambda_3 = G_\alpha - \frac{\partial G_\alpha}{\partial x_1^\alpha} x_1^\alpha - \frac{\partial G_\alpha}{\partial x_2^\alpha} x_2^\alpha = G_\beta - \frac{\partial G_\alpha}{\partial x_1^\alpha} x_1^\beta - \frac{\partial G_\alpha}{\partial x_2^\alpha} x_2^\beta = G_\gamma - \frac{\partial G_\alpha}{\partial x_1^\alpha} x_1^\gamma - \frac{\partial G_\alpha}{\partial x_2^\alpha} x_2^\gamma \tag{58}$$

$$\therefore G_\beta = G_\alpha - \frac{\partial G_\alpha}{\partial x_1^\alpha}(x_1^\alpha - x_1^\beta) - \frac{\partial G_\alpha}{\partial x_2^\alpha}(x_2^\alpha - x_2^\beta) \tag{59}$$

$$G_\gamma = G_\alpha - \frac{\partial G_\alpha}{\partial x_1^\alpha}(x_1^\alpha - x_1^\gamma) - \frac{\partial G_\alpha}{\partial x_2^\alpha}(x_2^\alpha - x_2^\gamma) \tag{60}$$

These represent equality of the grand potentials between pairs of phases $\alpha - \beta$ and $\alpha - \gamma$.

The system of Eqns. 53, 54, 56, 57, 59 & 60 represents 6 equations for 6 unknowns, which can be solved for the equilibrium plane containing the points $G_\alpha(x_1^\alpha, x_2^\alpha), G_\beta(x_1^\beta, x_2^\beta)$ and $G_\gamma(x_1^\gamma, x_2^\gamma)$.

Put it All Together

The code accompanying this document generates the equilibrium isothermobaric (constant T and P) phase diagram for a ternary alloy with three phases. The program iterates through system compositions (x_1, x_2) in the Gibbs simplex. At each test point, test energies are computed for

1. $G_\alpha(x_1, x_2)$
2. $G_\beta(x_1, x_2)$
3. $G_\gamma(x_1, x_2)$
4. $G_{\alpha\beta} = v_\alpha G_\alpha(x_1^\alpha, x_2^\alpha) + v_\beta G_\beta(x_1^\beta, x_2^\beta)$
5. $G_{\alpha\gamma} = v_\alpha G_\alpha(x_1^\alpha, x_2^\alpha) + v_\gamma G_\gamma$
6. $G_{\beta\gamma} = v_\beta G_\beta(x_1^\beta, x_2^\beta) + v_\gamma G_\gamma(x_1^\gamma, x_2^\gamma)$
7. $G_{\alpha\beta\gamma} = v_\alpha G_\alpha(x_1^\alpha, x_2^\alpha) + v_\beta G_\beta(x_1^\beta, x_2^\beta) + v_\gamma G_\gamma(x_1^\gamma, x_2^\gamma)$

The equilibrium phases and compositions corresponding to the system composition (x_1, x_2) are those corresponding to the minimum energy represented in that set of 7 possibilities, subject to the constraint that all endpoints must lie within the Gibbs simplex.