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Explicit constrained derivations and second-order analysis of Q-functions for flash specifications

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ABSTRACT

The present work develops an explicit constrained-optimization treatment of the Q-functions in Helmholtz-energy variables for the PSN, PHN, PTN, and SVN specifications. The actual independent-variable space is stated for each specification, the Lagrange multipliers are obtained directly from stationarity in those variables, and the resulting Q-functions are shown to recover the prescribed constraints and phase-equilibrium conditions. A second-order analysis then distinguishes the full Hessian of the unconstrained Q-function from the reduced Hessian relevant to the original constrained thermodynamic problem. We show that, on the admissible tangent space, the quadratic form of the Q-function Hessian coincides with that of the KKT Lagrangian.

1. Introduction

Phase equilibrium calculations are fundamental to numerous engineering disciplines, including chemical, petroleum, and geophysical applications. These calculations determine the distribution of species among coexisting phases under specified thermodynamic constraints. These constraints correspond to fixing different combinations of two thermodynamic state variables such as internal energy (U), enthalpy (H), pressure (P), temperature (T), entropy (S), volume (V), along with the total mole numbers ($N_1, N_2, \ldots, N_n$). These different combinations give rise to a family of so-called flash specifications. A comprehensive overview of these specifications is available in [1] and references therein.

Pressure-specified flash calculations include the PTN, PHN, and PSN specifications. The PTN flash, in which pressure, temperature, and total mole numbers are specified, is the standard isothermal–isobaric equilibrium calculation and forms the basis of most commercial process simulators (e.g., [2–4]). The PHN flash is formulated as the maximization of entropy at fixed pressure, enthalpy, and mole numbers [5–14]; it is relevant to adiabatic expansions, throttling processes, and compositional reservoir simulation of thermal recovery processes. Recent contributions address PHN phase stability [15], unified isenthalpic and isochoric flash calculations [16], nested three-phase calculations [17], direct entropy-maximization iterations [18], and an augmented-Q-function algorithm [19]. The PSN flash is formulated as the minimization of enthalpy at fixed pressure, entropy, and mole numbers [1,4,8,20,21]; it is relevant to reversible adiabatic operations and depressurization calculations, including compressors, pumps, turbines, and pipeline decompression.

Flash calculations with specified volume have received comparatively less attention. The VTN flash, defined by fixed volume, temperature, and mole numbers, is obtained by minimizing the Helmholtz free energy and is used to describe phase behavior in closed, isothermal vessels [1,22,23]. The UVN flash is formulated as the maximization of entropy at fixed internal energy, volume, and mole numbers [24–30]; it arises in dynamic simulations of distillation columns, multiphase pipe flow, tank filling, venting, and leakage from pressure vessels. The SVN flash is formulated as the minimization of internal energy at fixed entropy, volume, and mole numbers [20,21]. Although direct engineering applications of the SVN specification are less common, it is part of the general thermodynamic framework for state-function-based equilibrium calculations [12].

Michelsen [1] introduced Q-functions as a unified framework for state-function-based flash calculations. He showed that the solutions of PHN, PSN, UVN, SVN, and related flash specifications can be obtained as stationary points of suitable modified thermodynamic potentials, and identified the characteristic saddle-point structure of most of these Q-functions. He further proposed nested solution strategies in which the phase variables are minimized at fixed temperature and/or pressure while the remaining intensive variables are treated in an outer maximization. Both Gibbs-energy- and Helmholtz-energy-based forms were given; in particular, the Helmholtz formulation already contains the PSN, PHN, PTN, and SVN Q-functions considered here.

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Table 1
State function to be minimized for a given flash specification [1].

Specification	PTN	PHN	PSN	TVN	UVN	SVN
State function	G	$-S$	H	A	$-S$	U

Medeiros et al. [31] subsequently provided a general construction of Q-functions based on constrained optimization and Legendre transforms. Their analysis clarifies how the state function associated with the original flash specification is related to the thermodynamic potential whose natural variables are used in the numerical formulation, and extends the framework to open and reactive systems. They also discuss the second-order structure of Q-functions in terms of the convexity or concavity of thermodynamic potentials in extensive and intensive variable subspaces. The purpose of the present work is therefore not to introduce new Q-functions, but to complement this general framework with explicit, specification-resolved derivations in the Helmholtz-variable space actually used by a $T, V, \boldsymbol{N}$-based equation of state. Starting from the original constrained equilibrium problems, the Lagrange multipliers are obtained directly from the stationarity equations, with the required transformations between thermodynamic variable sets carried out explicitly. The resulting first-order conditions are then shown to recover the prescribed flash constraints together with mechanical and chemical equilibrium. This treatment makes explicit several intermediate steps that are compactly represented through thermodynamic conjugacy and Legendre transforms in the general construction of Medeiros et al.

Kumar and Rosen Esquivel [32] previously derived Michelsen's UVN Q-function from a Lagrangian in Helmholtz $T, V, \boldsymbol{N}$ variables by determining the energy-constraint multiplier from temperature stationarity. For PHN, Xu et al. [19] likewise obtained the Q-function by substituting the stationary value $1/T$ of the enthalpy-constraint multiplier into a fixed-pressure Lagrangian. The present PHN derivation keeps the phase volumes among the independent variables and makes the phase-pressure constraints explicit.

A second objective of the present work is to make the local second-order structure of these formulations explicit. In particular, we distinguish between the Hessian of the Q-function in the unrestricted computational variable space and the reduced Hessian relevant to the original constrained thermodynamic problem. It is shown that, although the full Q-function may be saddle-shaped, its quadratic form on perturbations satisfying the linearized flash constraints coincides with the KKT second variation of the original constrained problem. For the PSN formulation, this leads to an explicit inertia characterization of the full Helmholtz-variable Hessian and shows how its negative temperature direction is reconciled with nonnegative curvature on the PSN-admissible tangent space. Reduction along the fixed-$P, \boldsymbol{N}$ phase-equilibrium branch further recovers the negative temperature curvature underlying Michelsen's nested PSN-flash interpretation. Analogous results are developed for the remaining specifications with their respective sets of independent variables.

2. Decision variables

We formulate each flash specification as a constrained optimization problem in which the appropriate state function of a p-phase system is minimized, where p denotes the number of phases. The state functions associated with the flash specifications considered in this work are listed in Table 1.

Our presentation is based on the availability of a Helmholtz energy-based equation of state, i.e., we can evaluate thermodynamic properties explicitly if T, V, and $\boldsymbol{N}$ are available. Let $T \in \mathbb{R}_+$ be the common temperature. In all derivations, we will use the following notation: $V^{(k)}$ and $\mathbf{N}^{(k)} \in \mathbb{R}^n$ denote the volume and mole vector of phase k, respectively.

Define:

$$S^{(k)} = S(T, V^{(k)}, \mathbf{N}^{(k)}), \quad H^{(k)} = H(T, V^{(k)}, \mathbf{N}^{(k)}), \quad A^{(k)} = A(T, V^{(k)}, \mathbf{N}^{(k)}),$$
$$G^{(k)} = G(T, V^{(k)}, \mathbf{N}^{(k)}), \quad U^{(k)} = U(T, V^{(k)}, \mathbf{N}^{(k)}),$$

as the entropy, enthalpy, Helmholtz free energy, Gibbs free energy, and the internal energy of the k^{th} phase. The total quantities can be expressed as

$$V = \sum_{k=1}^{p} V^{(k)}, \quad S = \sum_{k=1}^{p} S^{(k)}, \quad H = \sum_{k=1}^{p} H^{(k)}, \quad A = \sum_{k=1}^{p} A^{(k)},$$
$$G = \sum_{k=1}^{p} G^{(k)}, \quad U = \sum_{k=1}^{p} U^{(k)}. \tag{1}$$

Denote by $\boldsymbol{V} := [V^{(1)}, \dots, V^{(p)}]^\top$ the phase-volume vector and by $\boldsymbol{N}^{(k)} \in \mathbb{R}^n_+$ the mole vector of phase k. The total mole balance is eliminated throughout the pressure-specified derivations by writing

$$\boldsymbol{N}^{(p)} = \boldsymbol{N}^{\text{spec}} - \sum_{k=1}^{p-1} \boldsymbol{N}^{(k)}.$$

It is important for both the first- and second-order analyses to distinguish the actual independent-variable spaces. For PSN and PHN we use

$$\boldsymbol{z}_P := \left[\boldsymbol{V}^\top, (\boldsymbol{N}^{(1)})^\top, \dots, (\boldsymbol{N}^{(p-1)})^\top\right]^\top, \qquad \boldsymbol{x}_P := \left[T, \boldsymbol{z}_P^\top\right]^\top.$$

For PTN, the specified temperature $T = T^{\text{spec}}$ is a parameter rather than an optimization variable, so the independent variables are only $\boldsymbol{z}_P$. For SVN, both the total mole and total volume balances are eliminated before optimization:

$$V^{(p)} = V^{\text{spec}} - \sum_{k=1}^{p-1} V^{(k)}, \qquad \boldsymbol{N}^{(p)} = \boldsymbol{N}^{\text{spec}} - \sum_{k=1}^{p-1} \boldsymbol{N}^{(k)},$$

and we use

$$\boldsymbol{z}_V := \left[V^{(1)}, \dots, V^{(p-1)}, (\boldsymbol{N}^{(1)})^\top, \dots, (\boldsymbol{N}^{(p-1)})^\top\right]^\top, \qquad \boldsymbol{x}_V := \left[T, \boldsymbol{z}_V^\top\right]^\top.$$

These definitions prevent a specified thermodynamic variable from being inadvertently included in the Hessian as a free optimization coordinate.

In the next section, we derive the pressure-specified Q-functions. The PSN and PHN cases share the variable vector $\boldsymbol{x}_P$; PTN is treated as the fixed-temperature limiting case.

3. Derivation of Q-function for PXN-flash

In this section, we discuss the general methodology for pressure-based flashes. We group these specifications as PXN flashes. For the PSN and PHN derivations below, $\mathbf{x}$ denotes the decision vector $\boldsymbol{x}_P$ defined above. A state function Y is minimized under the specification of pressure P, an extensive quantity X, and total mole numbers $\boldsymbol{N}$. The PTN case, for which temperature rather than an additional extensive quantity is specified, is treated separately with decision vector $\boldsymbol{z}_P$. The objective for the general PXN case is to optimize the total extensive quantity Y_{tot}

$$Y_{\text{tot}}(\mathbf{x}) := \sum_{k=1}^{p} Y(\mathbf{x}^{(k)})$$

subject to the following constraints:

1. **extensive constraint:**

$$C_X(\mathbf{x}) := \sum_{k=1}^{p} X(\mathbf{x}^{(k)}) - X^{\text{spec}} = 0,$$

2. **pressure constraints:**

$$C_P^{(k)}(\mathbf{x}) := P(\mathbf{x}^{(k)}) - P^{\text{spec}} = 0, \quad \text{for } k = 1, \dots, p.$$

Define the constraint vector:

$$\boldsymbol{C}(\mathbf{x}) := \begin{bmatrix} C_X(\mathbf{x}) \\ \boldsymbol{C}_P(\mathbf{x}) \end{bmatrix} \in \mathbb{R}^{p+1}, \quad \text{where} \quad \boldsymbol{C}_P(\mathbf{x}) := \begin{bmatrix} C_P^{(1)}(\mathbf{x}) \\ \vdots \\ C_P^{(p)}(\mathbf{x}) \end{bmatrix} \in \mathbb{R}^{p}. \tag{2}$$

The solution $\hat{\mathbf{x}}$ corresponds to the minimizer of the following constrained optimization problem:

$$\min_{\mathbf{x}} Y_{\text{tot}}(\mathbf{x}) \quad \text{subject to} \quad \boldsymbol{C}(\mathbf{x}) = 0.$$

The first-order conditions of this constrained optimization problem can be represented by the Lagrangian:

$$\mathcal{L}(\mathbf{x}, \lambda) = Y_{\text{tot}}(\mathbf{x}) + \lambda^{\top} \boldsymbol{C}(\mathbf{x}), \tag{3}$$

where λ are Lagrange multipliers defined as below

$$\lambda := \begin{bmatrix} \lambda_X \\ \lambda_P \end{bmatrix} \in \mathbb{R}^{p+1}, \tag{4}$$

where

1. $\lambda_X \in \mathbb{R}$: Lagrange multiplier for the extensive (or intensive) constraint
2. $\lambda_P := \begin{bmatrix} \lambda_P^{(1)} \\ \vdots \\ \lambda_P^{(p)} \end{bmatrix} \in \mathbb{R}^p$: Lagrange multipliers for pressure constraints.

Substituting Eqs. (2) and (4) into Eq. (3)

$$\begin{aligned} \mathcal{L}(\mathbf{x}, \lambda) &= Y_{\text{tot}}(\mathbf{x}) + \lambda_X C_X(\mathbf{x}) + \lambda_P^{\top} \boldsymbol{C}_P(\mathbf{x}), \\ &= \sum_{k=1}^{p} Y(\mathbf{x}^{(k)}) + \lambda_X \left(\sum_{k=1}^{p} X(\mathbf{x}^{(k)}) - X^{\text{spec}} \right) + \sum_{k=1}^{p} \lambda_P{}^{(k)} \left(P(\mathbf{x}^{(k)}) - P^{\text{spec}} \right) \end{aligned} \tag{5}$$

KKT conditions

The constrained minimum is then computed by requiring stationarity of the Lagrangian with respect to the optimization variables, together with satisfaction of the original constraints. The resulting Karush–Kuhn–Tucker (KKT) conditions are:

1. **Stationarity:**

$$\nabla_{\mathbf{x}} \mathcal{L}(\mathbf{x}, \lambda) = \mathbf{0}, \tag{6}$$

2. **Primal feasibility:**

$$\boldsymbol{C}(\mathbf{x}) = \mathbf{0}. \tag{7}$$

These equations form a coupled nonlinear system for the primal variables $\mathbf{x}$ and the Lagrange multipliers λ. In the present case, only equality constraints are considered, so the KKT conditions reduce to stationarity and primal feasibility. If inequality constraints were present, additional dual-feasibility and complementarity conditions would also be required.

3.1. Stationarity condition

The stationarity conditions are obtained by setting each element of the gradient equal to zero:

$$\left(\frac{\partial \mathcal{L}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} = 0 \tag{8}$$

$$\left(\frac{\partial \mathcal{L}}{\partial V^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} = 0 \quad \forall k = 1, \ldots, p \tag{9}$$

where $\boldsymbol{V}^{(\xi,k)} = \boldsymbol{V} \setminus V^{(k)}$ is the phase volumes vector not containing the volume of phase k.

Temperature gradient

Substituting the expression for the Lagrangian from Eq. (5) into Eq. (8) gives the temperature-gradient condition

$$\left(\frac{\partial \mathcal{L}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} = \sum_{k=1}^{p} \left(\frac{\partial Y^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} + \lambda_X \sum_{k=1}^{p} \left(\frac{\partial X^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} + \sum_{k=1}^{p} \lambda_P{}^{(k)} \left(\frac{\partial P^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} = 0. \tag{10}$$

Phasic volume gradient

Similarly, substituting the expression for the Lagrangian from Eq. (5) into Eq. (9) gives the volume-gradient condition

$$\begin{aligned} \left(\frac{\partial \mathcal{L}}{\partial V^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} &= \left(\frac{\partial Y^{(k)}}{\partial V^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} + \lambda_X \left(\frac{\partial X^{(k)}}{\partial V^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} \\ &\quad + \lambda_P{}^{(k)} \left(\frac{\partial P^{(k)}}{\partial V^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} = 0. \end{aligned} \tag{11}$$

$$\begin{aligned} \implies \lambda_P{}^{(k)} &= - \frac{\left(\frac{\partial Y^{(k)}}{\partial V^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} + \lambda_X \left(\frac{\partial X^{(k)}}{\partial V^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}}}{\left(\frac{\partial P^{(k)}}{\partial V^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}}} \\ &= - \left[\left(\frac{\partial Y^{(k)}}{\partial P^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} + \lambda_X \left(\frac{\partial X^{(k)}}{\partial P^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} \right]. \end{aligned} \tag{12}$$

Substituting Eq. (12) into Eq. (10), we get

$$\begin{aligned} \left(\frac{\partial \mathcal{L}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} &= \sum_{k=1}^{p} \left(\frac{\partial Y^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} + \lambda_X \sum_{k=1}^{p} \left(\frac{\partial X^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} - \sum_{k=1}^{p} \left[\left(\frac{\partial Y^{(k)}}{\partial P^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} \right. \\ &\quad \left. + \lambda_X \left(\frac{\partial X^{(k)}}{\partial P^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} \right] \left(\frac{\partial P^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}}. \end{aligned} \tag{13}$$

Rearranging the terms gives

$$\begin{aligned} \left(\frac{\partial \mathcal{L}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} &= \sum_{k=1}^{p} \left[\left(\frac{\partial Y^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} - \left(\frac{\partial Y^{(k)}}{\partial P^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} \left(\frac{\partial P^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} \right] \\ &\quad + \lambda_X \sum_{k=1}^{p} \left[\left(\frac{\partial X^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} - \left(\frac{\partial X^{(k)}}{\partial P^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} \left(\frac{\partial P^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} \right]. \end{aligned} \tag{14}$$

Using Eq. (F.4), we have $\left(\frac{\partial Z}{\partial T} \right)_{V_i} = \left(\frac{\partial Z}{\partial T} \right)_{P_i} + \left(\frac{\partial Z}{\partial P_i} \right)_{T} \left(\frac{\partial P_i}{\partial T} \right)_{V_i}$ for $Z = Y^{(k)}, X^{(k)}$ we get

$$\left(\frac{\partial X^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} - \left(\frac{\partial X^{(k)}}{\partial P^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} \left(\frac{\partial P^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} = \left(\frac{\partial X^{(k)}}{\partial T} \right)_{P^{(k)}} \tag{15}$$

and,

$$\left(\frac{\partial Y^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} - \left(\frac{\partial Y^{(k)}}{\partial P^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} \left(\frac{\partial P^{(k)}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} = \left(\frac{\partial Y^{(k)}}{\partial T} \right)_{P^{(k)}}. \tag{16}$$

Using Eqs. (15) and (16) into Eq. (14) gives:

$$\left(\frac{\partial \mathcal{L}}{\partial T} \right)_{\boldsymbol{V},\boldsymbol{N}} = \sum_{k=1}^{p} \left(\frac{\partial Y^{(k)}}{\partial T} \right)_{P^{(k)}} + \lambda_X \sum_{k=1}^{p} \left(\frac{\partial X^{(k)}}{\partial T} \right)_{P^{(k)}}. \tag{17}$$

Now, the stationarity condition $\frac{\partial \mathcal{L}}{\partial T} = 0$ yields

$$\lambda_X = - \frac{\sum_{k=1}^{p} \left(\frac{\partial Y^{(k)}}{\partial T} \right)_{P^{(k)}}}{\sum_{k=1}^{p} \left(\frac{\partial X^{(k)}}{\partial T} \right)_{P^{(k)}}} \tag{18}$$

.

PSN-flash: For PSN-flash, we need to minimize the enthalpy (H); putting $X = S$, $Y = H$ into Eq. (18) yields

$$\lambda_X = - \frac{\sum_{k=1}^{p} \left(\frac{\partial H^{(k)}}{\partial T} \right)_{P^{(k)}}}{\sum_{k=1}^{p} \left(\frac{\partial S^{(k)}}{\partial T} \right)_{P^{(k)}}} = - \sum_{k=1}^{p} C_P{}^{(k)} / \left(\sum_{k=1}^{p} C_P{}^{(k)} / T \right) = -T. \tag{19}$$

Substituting $X = S$, $Y = H, \lambda_X = -T$ into Eq. (12) yields

$$\lambda_P{}^{(k)} = - \left[\left(\frac{\partial H^{(k)}}{\partial P^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} - T \left(\frac{\partial S^{(k)}}{\partial P^{(k)}} \right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} \right].$$

Using identities (F.6) and (F.5) yields,

$$\lambda_P{}^{(k)} = -\left[V^{(k)} - T\left(\frac{\partial V^{(k)}}{\partial T}\right)_{P^{(k)}} + T\left(\frac{\partial V^{(k)}}{\partial T}\right)_{P^{(k)}}\right] = -V^{(k)}. \tag{20}$$

Substituting expressions (19) and (20) into Eq. (5), we get

$$\mathcal{L}^{(\mathrm{PSN})}(T,\boldsymbol{V},\boldsymbol{N}) = \sum_{k=1}^{p} H^{(k)} - T\left(\sum_{k=1}^{p} S^{(k)} - S^{\mathrm{spec}}\right) - \sum_{k=1}^{p} V^{(k)}\left(P^{(k)} - P^{\mathrm{spec}}\right). \tag{21}$$

Rearranging we get,

$$\mathcal{L}^{(\mathrm{PSN})}(T,\boldsymbol{V},\boldsymbol{N}) = \sum_{k=1}^{p}\left(\underbrace{H^{(k)} - TS^{(k)} - P^{(k)}V^{(k)}}_{=A^{(k)}}\right) + TS^{\mathrm{spec}} + P^{\mathrm{spec}}\sum_{k=1}^{p} V^{(k)} \tag{22}$$

$$\mathcal{L}^{(\mathrm{PSN})}(T,\boldsymbol{V},\boldsymbol{N}) = \sum_{k=1}^{p}\left(A^{(k)}\right) + TS^{\mathrm{spec}} + P^{\mathrm{spec}}\sum_{k=1}^{p} V^{(k)}. \tag{23}$$

Using Eq. (1), we can write Eq. (23) in a more compact form as

$$\boxed{\mathcal{L}^{(\mathrm{PSN})}(T,\boldsymbol{V},\boldsymbol{N}) = A + P^{\mathrm{spec}}V + TS^{\mathrm{spec}},} \tag{24}$$

which is the desired Q-function for PSN-flash.

PHN-flash: For the PHN-flash problem, we express entropy maximization as minimization of the sign-reversed entropy objective. Therefore, we set $X = H, \quad Y = -S$.

Eq. (18) then yields,

$$\lambda_X = -\frac{\sum_{k=1}^{p} -\left(\frac{\partial S^{(k)}}{\partial T}\right)_{P^{(k)}}}{\sum_{k=1}^{p}\left(\frac{\partial H^{(k)}}{\partial T}\right)_{P^{(k)}}} = \left(\sum_{k=1}^{p} C_P{}^{(k)}/T\right) / \sum_{k=1}^{p} C_P{}^{(k)} = 1/T.$$

The stationary enthalpy-constraint multiplier $1/T$ agrees with the fixed-pressure PHN derivation of Xu et al. [19]. Here the phase-pressure multipliers are also needed because the phase volumes remain independent variables.

Substituting $X = H,\ Y = -S, \lambda_X = 1/T$ in Eq. (12) yields

$$\lambda_P{}^{(k)} = -\left[-\left(\frac{\partial S^{(k)}}{\partial P^{(k)}}\right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} + 1/T\left(\frac{\partial H^{(k)}}{\partial P^{(k)}}\right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}}\right].$$

Using identities (F.6) and (F.5) yields,

$$\lambda_P{}^{(k)} = -\left[\left(\frac{\partial V^{(k)}}{\partial T}\right)_{P^{(k)}} + 1/T\left(V^{(k)} - T\left(\frac{\partial V^{(k)}}{\partial T}\right)_{P^{(k)}}\right)\right] = -\frac{V^{(k)}}{T}.$$

The final expressions for the Lagrange multipliers are

$$\boxed{\lambda_X = \frac{1}{T}, \quad \lambda_P{}^{(k)} = -\frac{V^{(k)}}{T}.} \tag{25}$$

Substituting these expressions in Lagrangian Equation (5), we get

$$\begin{aligned}\mathcal{L}(T,\boldsymbol{V},\boldsymbol{N}) &= \sum_{k=1}^{p} -S^{(k)} + \left(\sum_{k=1}^{p} H^{(k)} - H^{\mathrm{spec}}\right)/T - \sum_{k=1}^{p} V^{(k)}\left(P^{(k)} - P^{\mathrm{spec}}\right)/T \\ &= \sum_{k=1}^{p}\left[\frac{-TS^{(k)} + H^{(k)} - P^{(k)}V^{(k)}}{T}\right] - \frac{H^{\mathrm{spec}}}{T} + P^{\mathrm{spec}}\sum_{k=1}^{p}\frac{V^{(k)}}{T} \\ &= \frac{\sum_{k=1}^{p}\left(A^{(k)}\right) - H^{\mathrm{spec}} + P^{\mathrm{spec}}V}{T}.\end{aligned}$$

The final expression for the Lagrange function for PHN-flash becomes

$$\boxed{\mathcal{L}(T,\boldsymbol{V},\boldsymbol{N}) = \frac{A - H^{\mathrm{spec}} + P^{\mathrm{spec}}V}{T},} \tag{26}$$

which is the desired Q-function for PHN-flash.

PTN-flash: For PTN, $T = T^{\mathrm{spec}}$ is fixed and is not an optimization variable. The objective is the total Gibbs free energy, and the only nonlinear constraints introduced by the Helmholtz-variable representation are the phase-pressure conditions $P^{(k)} = P^{\mathrm{spec}}$. Thus the decision vector is $\boldsymbol{z}_P$, not $[T, \boldsymbol{z}_P^{\top}]^{\top}$. With $Y = G$ and no additional extensive constraint, the volume stationarity relation gives

$$\lambda_P{}^{(k)} = -\left(\frac{\partial G^{(k)}}{\partial P^{(k)}}\right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} \tag{27}$$

Using identity (F.11) into Eq. (27), we get

$$\lambda_P{}^{(k)} = -V^{(k)}. \tag{28}$$

Substituting Eq. (28) and $\lambda_X = 0$ into Eq. (5), we get

$$\begin{aligned}\mathcal{L}(T,\boldsymbol{V},\boldsymbol{N}) &= \sum_{k=1}^{p} G^{(k)} - \sum_{k=1}^{p} V^{(k)}\left(P^{(k)} - P^{\mathrm{spec}}\right) \\ &= \sum_{k=1}^{p}\left(\underbrace{G^{(k)} - P^{(k)}V^{(k)}}_{=A^{(k)}}\right) + P^{\mathrm{spec}}\sum_{k=1}^{p} V^{(k)}.\end{aligned} \tag{29}$$

The final expression for the Lagrange function in PTN-flash becomes

$$\boxed{\mathcal{L}(T,\boldsymbol{V},\boldsymbol{N}) = A + P^{\mathrm{spec}}V} \tag{30}$$

3.2. First-order analysis of the Q-function for PSN flash

The Q-function formulation recasts the constrained enthalpy-minimization problem into an unconstrained saddle-point problem. The Q-function is not a conventional Lagrangian: it contains no explicit multipliers enforcing the fixed-entropy and fixed-pressure constraints of the PSN specification. It is, therefore, not immediately evident that the stationary points of Q-function (24) correspond to the thermodynamic equilibrium state. Furthermore, enthalpy is naturally expressed as a function of pressure, entropy, and mole numbers, $H = H(P,S,\boldsymbol{N})$, whereas the Q-function is formulated in the variables $(T,V,\boldsymbol{N})$ native to a Helmholtz-energy-based equation of state. It must therefore be shown that stationarity of the Q-function with respect to $(T,V,\boldsymbol{N})$ recovers the same equilibrium state that constrained minimization of $H(P,S,\boldsymbol{N})$ identifies under the PSN specification.

We verify this equivalence by examining the first-order stationarity conditions of Eq. (24) and showing that they simultaneously reproduce:

1. the prescribed entropy constraint;
2. equality of pressure across all phases, with each phase pressure equal to the specified pressure P^{spec};
3. equality of the chemical potential of each component across all coexisting phases.

3.2.1. Stationarity with respect to temperature

Differentiating the Q-function (23) with respect to T, we obtain:

$$\left(\frac{\partial \mathcal{L}^{(\mathrm{PSN})}}{\partial T}\right)_{\boldsymbol{V},\boldsymbol{N}} = S^{\mathrm{spec}} + \sum_{k=1}^{p}\underbrace{\left(\frac{\partial A^{(k)}}{\partial T}\right)_{\boldsymbol{V},\boldsymbol{N}}}_{-S^{(k)}}, \tag{31}$$

Setting the derivative to zero gives:

$$\left(\frac{\partial \mathcal{L}^{(\mathrm{PSN})}}{\partial T}\right)_{\boldsymbol{V},\boldsymbol{N}} = 0 \implies S^{\mathrm{spec}} = \sum_{k=1}^{p} S^{(k)},$$

thus, recovering the entropy constraint.

3.2.2. Stationarity with respect to volume

Next, differentiating with respect to $V^{(k)}$:

$$\left(\frac{\partial \mathcal{L}^{(\mathrm{PSN})}}{\partial V^{(k)}}\right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}} = \underbrace{\left(\frac{\partial A^{(k)}}{\partial V^{(k)}}\right)_{T,\boldsymbol{V}^{(\xi,k)},\boldsymbol{N}}}_{-P^{(k)}} + P^{\mathrm{spec}}, \tag{32}$$

Setting this derivative to zero implies:

$$P^{(1)} = \cdots = P^{(p)} = P^{\mathrm{spec}} \quad \forall k = 1,\ldots,p,$$

which enforces equality of pressure across all phases.

3.2.3. Stationarity with respect to mole numbers

Next, we rewrite Eq. (23) in the following form:

$$\mathcal{L}^{(\mathrm{PSN})}(T,\boldsymbol{V},\boldsymbol{N}) = \sum_{k=1}^{p-1}\left(A(T,V^{(k)},\boldsymbol{N}^{(k)}) + P^{\mathrm{spec}}V^{(k)}\right) + \left(A(T,V^{(p)},\boldsymbol{N}^{(p)}) + P^{\mathrm{spec}}V^{(p)}\right) + TS^{\mathrm{spec}}, \tag{33}$$

where $\boldsymbol{N}^{(p)} := \{N_1^{\mathrm{spec}} - \sum_{k=1}^{p-1} N_1^{(k)}, \dots, N_n^{\mathrm{spec}} - \sum_{k=1}^{p-1} N_n^{(k)}\}$.

Finally, differentiating with respect to the mole number of component i in phase k, i.e., $\boldsymbol{N}_i^{(k)}$ for $i = 1,\dots,n$ and $k = 1,\dots,p-1$, with the other independent variables held fixed, we obtain:

$$\left(\frac{\partial \mathcal{L}^{(\mathrm{PSN})}}{\partial \boldsymbol{N}_i^{(k)}}\right) = \underbrace{\left(\frac{\partial A(T,V^{(k)},\boldsymbol{N}^{(k)})}{\partial \boldsymbol{N}_i^{(k)}}\right)_{T,V^{(k)},N_{j\neq i}^{(k)}}}_{\mu_i^{(k)}} - \underbrace{\left(\frac{\partial A(T,V^{(p)},\boldsymbol{N}^{(p)})}{\partial \boldsymbol{N}_i^{(p)}}\right)_{T,V^{(p)},N_{j\neq i}^{(p)}}}_{\mu_i^{(p)}}, \tag{34}$$

Setting this to zero yields:

$$\mu_i^{(1)} = \mu_i^{(2)} = \cdots = \mu_i^{(p)} \quad \forall i = 1,\dots,n, \tag{35}$$

thus confirming equality of chemical potentials for all components across phases.

Hence, the stationarity conditions of the Q-function are consistent with thermodynamic equilibrium under the PSN constraints. The thermodynamic consistency of PHN and PTN flash can also be established using an analogous approach. We now proceed to the derivation of volume-based specification.

4. Derivation of Q-function for SVN-flash

Three types of volume-based flash specifications are commonly considered: VTN, UVN, and SVN. In the VTN flash formulation, thermodynamic equilibrium is obtained by minimizing the total Helmholtz free energy at fixed temperature, volume, and mole numbers, which results in an unconstrained optimization problem. The UVN flash formulation has been treated in detail elsewhere; the reader is referred to [32] for its derivation and numerical implementation.

In this paper, we focus on the remaining volume-based formulation: the SVN-flash and provide a detailed derivation of the associated Q-function. Under the SVN specification, equilibrium corresponds to minimization of the total internal energy at fixed total entropy, total volume, and component mole numbers. We first eliminate the linear total-volume and total-mole balances using the residual phase definitions given above. The only remaining nonlinear equality constraint is then the specified total entropy. For a p-phase system, consider the Lagrangian:

$$\mathcal{L}(T,\boldsymbol{V},\boldsymbol{N}) = \sum_{k=1}^{p} U^{(k)} + \lambda_S\left(\sum_{k=1}^{p} S^{(k)} - S^{\mathrm{spec}}\right) \tag{36}$$

4.1. Stationarity condition

The temperature and volume stationarity conditions, with the other independent variables held fixed, are

$$\left(\frac{\partial \mathcal{L}}{\partial T}\right)_{V,\boldsymbol{N}} = 0, \tag{37a}$$

$$\left(\frac{\partial \mathcal{L}}{\partial V^{(k)}}\right) = 0 \quad \forall k = 1,\ \cdots,\ p-1 \quad . \tag{37b}$$

Temperature Gradient

$$\left(\frac{\partial \mathcal{L}}{\partial T}\right)_{V,\boldsymbol{N}} = \left[\sum_{k=1}^{p}\left(\frac{\partial U^{(k)}}{\partial T}\right)_{V,\boldsymbol{N}}\right] + \lambda_S\left[\sum_{k=1}^{p}\left(\frac{\partial S^{(k)}}{\partial T}\right)_{V,\boldsymbol{N}}\right]. \tag{38}$$

Setting $\left(\frac{\partial \mathcal{L}}{\partial T}\right)_{V,\boldsymbol{N}} = 0 \implies \boxed{\lambda_S = -\left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{N}} = -T.}$ (39)

Substituting this in Eq. (36) yields

$$\mathcal{L}(T,\boldsymbol{V},\boldsymbol{N}) = \sum_{k=1}^{p} U^{(k)} - T\left(\sum_{k=1}^{p} S^{(k)} - S^{\mathrm{spec}}\right) = \sum_{k=1}^{p}\left(U^{(k)} - TS^{(k)}\right) + TS^{\mathrm{spec}} \tag{40}$$

The final expression for the Lagrange function for SVN-flash becomes

$$\boxed{\mathcal{L}(T,\boldsymbol{V},\boldsymbol{N}) = A + TS^{\mathrm{spec}},} \tag{41}$$

which is the desired Q-function for the SVN-flash.

4.2. First-order analysis of Q-function for SVN flash

Similar to the PSN-flash, the Q-function associated with the SVN specification is not a Lagrangian in the classical sense. Consequently, it is not a priori clear that the stationary points of the SVN Q-function correspond to thermodynamic equilibrium. For completeness, we therefore analyze the stationarity conditions of the associated Lagrangian and show that they recover the thermodynamic equilibrium under prescribed constraints.

The Lagrangian (40) associated with the constrained minimization of the total internal energy at fixed total entropy is given by

$$\mathcal{L}(T,V,N) = \sum_{k=1}^{p} U(T,V^{(k)},N^{(k)}) - T\left(\sum_{k=1}^{p} S(T,V^{(k)},N^{(k)}) - S^{\mathrm{spec}}\right). \tag{42}$$

4.2.1. Stationarity with respect to temperature

Taking the partial derivative of $\mathcal{L}$ with respect to T, while keeping $V^{(k)}$ and $N^{(k)}$ fixed for all k, yields

$$\frac{\partial \mathcal{L}}{\partial T} = \sum_{k=1}^{p}\frac{\partial U^{(k)}}{\partial T} - \left(\sum_{k=1}^{p} S^{(k)} - S^{\mathrm{spec}}\right) - T\sum_{k=1}^{p}\frac{\partial S^{(k)}}{\partial T}. \tag{43}$$

Substituting the thermodynamic identity

$$\left(\frac{\partial U^{(k)}}{\partial T}\right)_{V,N} = T\left(\frac{\partial S^{(k)}}{\partial T}\right)_{V,N} \tag{44}$$

into Eq. (43) leads to the exact cancellation of the temperature-dependent terms, yielding:

$$\frac{\partial \mathcal{L}}{\partial T} = -\left(\sum_{k=1}^{p} S^{(k)} - S^{\mathrm{spec}}\right). \tag{45}$$

The stationarity condition $\partial\mathcal{L}/\partial T = 0$ therefore enforces

$$\sum_{k=1}^{p} S^{(k)} = S^{\mathrm{spec}}, \tag{46}$$

which shows that the specified total entropy is the sum of entropies of the individual phases at equilibrium.

4.2.2. Stationarity with respect to volume

Rewriting the Lagrangian by separating the first $p-1$ phases from the residual pth phase as

$$\mathcal{L}(T,\boldsymbol{V},\boldsymbol{N}) = \sum_{k=1}^{p-1} U(T,V^{(k)},N^{(k)}) + U(T,V^{(p)},N^{(p)}) - T\left(\sum_{k=1}^{p-1} S(T,V^{(k)},N^{(k)}) + S(T,V^{(p)},N^{(p)}) - S^{\mathrm{spec}}\right), \tag{47}$$

where the residual phase quantities are defined by the total balance relations

$$V^{(p)} := V^{\mathrm{spec}} - \sum_{k=1}^{p-1} V^{(k)}, \qquad N^{(p)} := N^{\mathrm{spec}} - \sum_{k=1}^{p-1} N^{(k)}. \tag{48}$$

The partial derivative of $\mathcal{L}$ (47) with respect to $V^{(k)}$, for $k = 1, \dots, p-1$, is obtained using the chain rule,

$$\frac{\partial \mathcal{L}}{\partial V^{(k)}} = \frac{\partial U^{(k)}}{\partial V^{(k)}} - T\frac{\partial S^{(k)}}{\partial V^{(k)}} + \frac{\partial U^{(p)}}{\partial V^{(p)}}\frac{\partial V^{(p)}}{\partial V^{(k)}} - T\frac{\partial S^{(p)}}{\partial V^{(p)}}\frac{\partial V^{(p)}}{\partial V^{(k)}}. \tag{49}$$

Since $\partial V^{(p)}/\partial V^{(k)} = -1$, this reduces to

$$\frac{\partial \mathcal{L}}{\partial V^{(k)}} = \left(\frac{\partial U^{(k)}}{\partial V^{(k)}} - T\frac{\partial S^{(k)}}{\partial V^{(k)}}\right) - \left(\frac{\partial U^{(p)}}{\partial V^{(p)}} - T\frac{\partial S^{(p)}}{\partial V^{(p)}}\right). \tag{50}$$

Using the thermodynamic identity $(\partial U/\partial V)_{T,N} = T(\partial S/\partial V)_{T,N} - P$, one finally obtains

$$\frac{\partial \mathcal{L}}{\partial V^{(k)}} = -P^{(k)} + P^{(p)}. \tag{51}$$

The stationarity condition $\partial \mathcal{L}/\partial V^{(k)} = 0$ therefore enforces

$$P^{(k)} = P^{(p)}, \qquad k = 1, \dots, p-1, \tag{52}$$

which expresses mechanical equilibrium between all phases.

4.2.3. Stationarity with respect to mole numbers

The partial derivative of the Lagrangian with respect to the mole number $N_i^{(k)}$ of component i in phase k, for $k = 1, \dots, p-1$, is obtained by applying the chain rule,

$$\frac{\partial \mathcal{L}}{\partial N_i^{(k)}} = \frac{\partial U^{(k)}}{\partial N_i^{(k)}} - T\frac{\partial S^{(k)}}{\partial N_i^{(k)}} + \frac{\partial U^{(p)}}{\partial N_i^{(p)}}\frac{\partial N_i^{(p)}}{\partial N_i^{(k)}} - T\frac{\partial S^{(p)}}{\partial N_i^{(p)}}\frac{\partial N_i^{(p)}}{\partial N_i^{(k)}}. \tag{53}$$

From the material balance constraint $N_i^{(p)} := N_i^{\mathrm{spec}} - \sum_{k=1}^{p-1} N_i^{(k)}$, it follows that $\partial N_i^{(p)}/\partial N_i^{(k)} = -1$. Hence,

$$\frac{\partial \mathcal{L}}{\partial N_i^{(k)}} = \left(\frac{\partial U^{(k)}}{\partial N_i^{(k)}} - T\frac{\partial S^{(k)}}{\partial N_i^{(k)}}\right) - \left(\frac{\partial U^{(p)}}{\partial N_i^{(p)}} - T\frac{\partial S^{(p)}}{\partial N_i^{(p)}}\right). \tag{54}$$

Using the fundamental thermodynamic identity $(\partial U/\partial N_i)_{T,V} = T(\partial S/\partial N_i)_{T,V} + \mu_i$, one obtains

$$\frac{\partial \mathcal{L}}{\partial N_i^{(k)}} = \mu_i^{(k)} - \mu_i^{(p)}. \tag{55}$$

The stationarity condition $\partial \mathcal{L}/\partial N_i^{(k)} = 0$ therefore implies

$$\mu_i^{(k)} = \mu_i^{(p)}, \qquad i = 1, \dots, n, \quad k = 1, \dots, p-1, \tag{56}$$

which expresses chemical equilibrium for every component between all phases.

5. Second-order structure and constrained stability

Michelsen [1] identified the characteristic saddle-point structure of the Q-functions, with positive curvature along phase-splitting directions and negative curvature along temperature and/or pressure directions, and derived the reduced heat-capacity curvature underlying the nested formulation. Medeiros et al. [31] subsequently formulated a generic Q-function Hessian and interpreted its sign structure in terms of extensive and intensive thermodynamic subspaces. In the present work, we make this connection explicit for each Helmholtz-based flash specification: using its actual set of independent optimization variables, we relate the full Q-function Hessian directly to the constrained second variation of the corresponding underlying thermodynamic minimization problem.

The Q-functions remove the nonlinear flash constraints from the equations that are solved, but the underlying thermodynamic equilibrium problem remains a constrained minimization problem. Consequently, two different second-order objects must be distinguished: the full Hessian of the Q-function in its free variables, which describes the local saddle geometry used by Newton or nested algorithms, and the reduced Hessian of the original constrained problem on physically admissible perturbations.

5.1. Relation between the Q-function Hessian and the constrained second variation

Consider a regular equality-constrained problem

$$\min_{\boldsymbol{x}} \; f(\boldsymbol{x}), \qquad \boldsymbol{c}(\boldsymbol{x}) = \boldsymbol{0}, \tag{57}$$

with Lagrangian

$$\mathcal{L}(\boldsymbol{x}, \boldsymbol{\lambda}) = f(\boldsymbol{x}) + \boldsymbol{\lambda}^{\top}\boldsymbol{c}(\boldsymbol{x}). \tag{58}$$

Let $(\boldsymbol{x}^{\star}, \boldsymbol{\lambda}^{\star})$ satisfy the KKT conditions, and let a Q-function be obtained by replacing the equilibrium multipliers by smooth functions of the thermodynamic variables,

$$Q(\boldsymbol{x}) = f(\boldsymbol{x}) + \hat{\boldsymbol{\lambda}}(\boldsymbol{x})^{\top}\boldsymbol{c}(\boldsymbol{x}), \qquad \hat{\boldsymbol{\lambda}}(\boldsymbol{x}^{\star}) = \boldsymbol{\lambda}^{\star}. \tag{59}$$

This is precisely the situation in the constructions above: for example, in PSN, $\hat{\lambda}_S = -T$ and $\hat{\lambda}_P^{(k)} = -V^{(k)}$. Since $\boldsymbol{c}(\boldsymbol{x}^{\star}) = \boldsymbol{0}$, the Q-function and the KKT Lagrangian have the same first derivative at the solution. Their full Hessians are not generally identical because the promoted multipliers vary with $\boldsymbol{x}$. However, for every tangent perturbation $\boldsymbol{d}$ satisfying

$$\boldsymbol{J}_c(\boldsymbol{x}^{\star})\boldsymbol{d} = \boldsymbol{0}, \tag{60}$$

the additional cross terms vanish and

$$\boxed{\boldsymbol{d}^{\top}\nabla^2 Q(\boldsymbol{x}^{\star})\boldsymbol{d} = \boldsymbol{d}^{\top}\nabla^2_{\boldsymbol{xx}}\mathcal{L}(\boldsymbol{x}^{\star}, \boldsymbol{\lambda}^{\star})\boldsymbol{d}.} \tag{61}$$

Equivalently, if the columns of $\boldsymbol{Z}$ span $\ker \boldsymbol{J}_c(\boldsymbol{x}^{\star})$ (see Appendix B), then

$$\boxed{\boldsymbol{Z}^{\top}\nabla^2 Q(\boldsymbol{x}^{\star})\boldsymbol{Z} = \boldsymbol{Z}^{\top}\nabla^2_{\boldsymbol{xx}}\mathcal{L}(\boldsymbol{x}^{\star}, \boldsymbol{\lambda}^{\star})\boldsymbol{Z}.} \tag{62}$$

Thus the second-order necessary condition for a locally stable constrained flash solution is nonnegativity of this reduced matrix, not positive semidefiniteness of the full Q-function Hessian. Strict positivity on the tangent space gives the corresponding standard sufficient condition for a strict local constrained minimum. At phase boundaries, where nonnegativity constraints on phase or component amounts become active, the tangent space must be replaced by the KKT critical cone.

5.2. Helmholtz curvature in the reduced extensive variables

For phase k, define the extensive vector

$$\boldsymbol{y}^{(k)} := \left[V^{(k)}, (\boldsymbol{N}^{(k)})^{\top}\right]^{\top}, \qquad \boldsymbol{H}_A^{(k)} := \nabla^2_{\boldsymbol{y}^{(k)}\boldsymbol{y}^{(k)}} A^{(k)}(T, \boldsymbol{y}^{(k)}). \tag{63}$$

At fixed temperature, local mechanical and diffusive stability of a homogeneous phase requires nonnegative Helmholtz curvature on admissible extensive perturbations; in particular,

$$A^{(k)}_{V^{(k)}V^{(k)}} = -\left(\frac{\partial P^{(k)}}{\partial V^{(k)}}\right)_{T,N^{(k)}} > 0 \tag{64}$$

away from mechanical degeneracy. More generally, $\boldsymbol{H}_A^{(k)} \succeq \boldsymbol{0}$ for a locally stable homogeneous phase, with possible null directions associated with extensivity or coexistence degeneracy. Because the total-mole and, where applicable, total-volume balances are eliminated by affine maps, the fixed-temperature Hessian in the retained coordinates has the form

$$\boldsymbol{K} = \boldsymbol{R}^{\top}\,\mathrm{diag}\left(\boldsymbol{H}_A^{(1)}, \dots, \boldsymbol{H}_A^{(p)}\right)\boldsymbol{R} \succeq \boldsymbol{0}, \tag{65}$$

where $\boldsymbol{R}$ maps a retained perturbation to the corresponding phase-volume and phase-mole perturbations. Eq. (65) makes explicit that the relevant composition/volume curvature is the Helmholtz curvature projected onto the linear balance subspace.

5.3. PSN flash

For PSN, the independent variables are $\boldsymbol{x}_P = [T, \boldsymbol{z}_P^\top]^\top$, where $\boldsymbol{z}_P$ collects the independent phase volumes and mole numbers after elimination of the total mole-balance constraints. The Q-function is

$$Q_{\mathrm{PSN}} = \overline{A}(T, \boldsymbol{z}_P) + P^{\mathrm{spec}} V + T S^{\mathrm{spec}}. \tag{66}$$

Since $P^{\mathrm{spec}} V$ is linear in the phase-volume variables and $T S^{\mathrm{spec}}$ is linear in T, both terms have zero Hessian in the chosen optimization variables,

$$\boxed{\nabla^2 Q^\star_{\mathrm{PSN}} = \nabla^2 \overline{A}^\star = \begin{bmatrix} a & \boldsymbol{g}^\top \\ \boldsymbol{g} & \boldsymbol{K} \end{bmatrix}.} \tag{67}$$

Here

$$a = \overline{A}^\star_{TT} = -\left(\frac{\partial S}{\partial T}\right)^\star_{\boldsymbol{z}_P} = -\frac{C^\star_{V,\mathrm{tot}}}{T^\star} < 0, \tag{68}$$

$$\boldsymbol{g} = \nabla_{\boldsymbol{z}_P} \overline{A}^\star_T, \qquad \boldsymbol{K} = \nabla^2_{\boldsymbol{z}_P \boldsymbol{z}_P} \overline{A}^\star, \tag{69}$$

where $C_{V,\mathrm{tot}} = \sum_k C_V^{(k)}$. For a locally stable fixed-temperature phase state, the Helmholtz curvature with respect to the admissible phase variables is nonnegative, so that

$$\boldsymbol{K} \succeq \boldsymbol{0}. \tag{70}$$

A congruence transformation eliminates the temperature–phase-variable cross block without changing the inertia:

$$\nabla^2 Q^\star_{\mathrm{PSN}} \sim \begin{bmatrix} a & \boldsymbol{0}^\top \\ \boldsymbol{0} & \boldsymbol{K} - \frac{1}{a}\boldsymbol{g}\boldsymbol{g}^\top \end{bmatrix} = \begin{bmatrix} a & \boldsymbol{0}^\top \\ \boldsymbol{0} & \boldsymbol{K} + \frac{1}{|a|}\boldsymbol{g}\boldsymbol{g}^\top \end{bmatrix}. \tag{71}$$

Because $\boldsymbol{K} \succeq \boldsymbol{0}$ and $\boldsymbol{g}\boldsymbol{g}^\top \succeq \boldsymbol{0}$, the lower block is positive semidefinite, whereas $a < 0$. Sylvester's law of inertia (see Appendix D) therefore gives

$$\boxed{n_-\left(\nabla^2 Q^\star_{\mathrm{PSN}}\right) = 1.} \tag{72}$$

Thus the unrestricted PSN Q-function has exactly one negative-curvature direction.

More precisely, let $m = \dim \boldsymbol{z}_P$ and define

$$r := \dim\left(\ker \boldsymbol{K} \cap \boldsymbol{g}^\perp\right), \tag{73}$$

where r is the number of independent zero-curvature directions of $\boldsymbol{K}$ that are also orthogonal to the temperature-coupling vector $\boldsymbol{g}$. Then, with $\mathrm{In} = (n_+, n_-, n_0)$,

$$\boxed{\mathrm{In}\left(\nabla^2 Q^\star_{\mathrm{PSN}}\right) = (m - r, 1, r).} \tag{74}$$

Hence a locally fixed-temperature-stable interior PSN state is saddle-shaped in the full Q-function variable space, with one negative direction and possible zero modes at degenerate states.

Curvature on the PSN-admissible space

The full-space saddle character does not contradict the constrained enthalpy-minimum principle underlying the PSN flash. The original PSN problem allows only perturbations that preserve the specified entropy and phase-pressure constraints. Define

$$\boldsymbol{c}_{\mathrm{PSN}}(\boldsymbol{x}_P) := \left[S - S^{\mathrm{spec}},\ P^{(1)} - P^{\mathrm{spec}},\ \ldots,\ P^{(p)} - P^{\mathrm{spec}}\right]^\top. \tag{75}$$

If $\boldsymbol{Z}_{\mathrm{PSN}}$ spans the null space of the Jacobian of (75), then the admissible first-order perturbations lie in $\mathrm{Range}(\boldsymbol{Z}_{\mathrm{PSN}})$. The corresponding local second-order condition is

$$\boxed{\boldsymbol{Z}_{\mathrm{PSN}}^\top \nabla^2 Q^\star_{\mathrm{PSN}} \boldsymbol{Z}_{\mathrm{PSN}} \succeq \boldsymbol{0},} \tag{76}$$

which, by (62), is exactly the KKT reduced-Hessian condition for the original constrained enthalpy minimization.

The role of the entropy constraint can be seen directly. Consider a small perturbation $(\delta T, \delta \boldsymbol{z}_P)$. To first order,

$$\delta S = S^\star_T \, \delta T + (\nabla_{\boldsymbol{z}_P} S^\star)^\top \delta \boldsymbol{z}_P. \tag{77}$$

Since $\overline{A}_T = -S$, Eqs. (68)–(69) imply

$$a = -S^\star_T, \qquad \boldsymbol{g} = -\nabla_{\boldsymbol{z}_P} S^\star. \tag{78}$$

Therefore an entropy-preserving perturbation, $\delta S = 0$, satisfies

$$\boxed{a\,\delta T + \boldsymbol{g}^\top \delta \boldsymbol{z}_P = 0.} \tag{79}$$

Thus temperature cannot vary independently along the PSN constraint surface. Solving (79) for δT gives

$$\delta T = -\frac{\boldsymbol{g}^\top \delta \boldsymbol{z}_P}{a}. \tag{80}$$

The quadratic form associated with the full Hessian (67) is

$$\begin{aligned} \delta^2 Q_{\mathrm{PSN}} &= \begin{bmatrix} \delta T & \delta \boldsymbol{z}_P^\top \end{bmatrix} \begin{bmatrix} a & \boldsymbol{g}^\top \\ \boldsymbol{g} & \boldsymbol{K} \end{bmatrix} \begin{bmatrix} \delta T \\ \delta \boldsymbol{z}_P \end{bmatrix} \\ &= a(\delta T)^2 + 2\delta T\, \boldsymbol{g}^\top \delta \boldsymbol{z}_P + \delta \boldsymbol{z}_P^\top \boldsymbol{K} \delta \boldsymbol{z}_P. \end{aligned} \tag{81}$$

Substituting the entropy-preserving relation (80) gives

$$\begin{aligned} \delta^2 Q_{\mathrm{PSN}} &= a\left(-\frac{\boldsymbol{g}^\top \delta \boldsymbol{z}_P}{a}\right)^2 + 2\left(-\frac{\boldsymbol{g}^\top \delta \boldsymbol{z}_P}{a}\right) \boldsymbol{g}^\top \delta \boldsymbol{z}_P + \delta \boldsymbol{z}_P^\top \boldsymbol{K} \delta \boldsymbol{z}_P \\ &= \frac{(\boldsymbol{g}^\top \delta \boldsymbol{z}_P)^2}{a} - \frac{2(\boldsymbol{g}^\top \delta \boldsymbol{z}_P)^2}{a} + \delta \boldsymbol{z}_P^\top \boldsymbol{K} \delta \boldsymbol{z}_P \\ &= -\frac{1}{a}(\boldsymbol{g}^\top \delta \boldsymbol{z}_P)^2 + \delta \boldsymbol{z}_P^\top \boldsymbol{K} \delta \boldsymbol{z}_P. \end{aligned} \tag{82}$$

Since $a < 0$,

$$-\frac{1}{a} = \frac{1}{|a|}, \tag{83}$$

and

$$(\boldsymbol{g}^\top \delta \boldsymbol{z}_P)^2 = \delta \boldsymbol{z}_P^\top \boldsymbol{g}\boldsymbol{g}^\top \delta \boldsymbol{z}_P. \tag{84}$$

Consequently,

$$\boxed{\delta^2 Q_{\mathrm{PSN}} = \delta \boldsymbol{z}_P^\top \left(\boldsymbol{K} + \frac{1}{|a|}\boldsymbol{g}\boldsymbol{g}^\top\right) \delta \boldsymbol{z}_P.} \tag{85}$$

Thus, when $\boldsymbol{K} \succeq \boldsymbol{0}$, the Q-function curvature is nonnegative on the entropy-preserving hyperplane. The complete PSN admissible space is smaller still, because the phase-pressure constraints additionally require

$$\delta P^{(k)} = 0, \qquad k = 1, \ldots, p. \tag{86}$$

These linearized pressure conditions further restrict the entropy-preserving perturbations. Hence the two statements refer to different spaces: the unrestricted Q-function is saddle-shaped, while its curvature along perturbations admissible for the original PSN problem is nonnegative.

Reduced temperature curvature

When $\boldsymbol{K} \succ \boldsymbol{0}$, the fixed-$P^{\mathrm{spec}}, \boldsymbol{N}^{\mathrm{spec}}$ phase-equilibrium conditions define a smooth local branch $\overline{\boldsymbol{z}}_P(T)$ satisfying

$$\nabla_{\boldsymbol{z}_P} Q_{\mathrm{PSN}}\left(T, \overline{\boldsymbol{z}}_P(T)\right) = \boldsymbol{0}. \tag{87}$$

The implicit-function theorem then gives

$$\frac{\mathrm{d}\overline{\boldsymbol{z}}_P}{\mathrm{d}T} = -\boldsymbol{K}^{-1}\boldsymbol{g}. \tag{88}$$

Defining the Q-function restricted to this equilibrated branch as

$$\overline{Q}_{\mathrm{PSN}}(T) := Q_{\mathrm{PSN}}\left(T, \overline{\boldsymbol{z}}_P(T)\right), \tag{89}$$

its stationary condition reduces to

$$\overline{Q}'_{\mathrm{PSN}}(T) = S^{\mathrm{spec}} - S_{\mathrm{br}}(T), \tag{90}$$

so that the PSN temperature $T^\star$ satisfies $S_{\mathrm{br}}(T^\star) = S^{\mathrm{spec}}$.

The corresponding reduced temperature curvature is

$$\boxed{\overline{Q}''_{\mathrm{PSN}}(T^\star) = a - \boldsymbol{g}^\top \boldsymbol{K}^{-1}\boldsymbol{g} = -\frac{C^\star_{P,\mathrm{br}}}{T^\star} < 0,} \tag{91}$$

for $C^\star_{P,\mathrm{br}} > 0$, where $C_{P,\mathrm{br}}$ denotes the heat capacity along the local fixed-P^{spec}, $\boldsymbol{N}^{\mathrm{spec}}$ phase-equilibrium branch. If this branch is the globally stable one, $C_{P,\mathrm{br}}$ is the equilibrium heat capacity $C_{P,\mathrm{eq}}$.

Using $a = -C^\star_{V,\mathrm{tot}}/T^\star$ gives

$$\boxed{C^\star_{P,\mathrm{br}} = C^\star_{V,\mathrm{tot}} + T^\star \boldsymbol{g}^\top \boldsymbol{K}^{-1}\boldsymbol{g}.} \tag{92}$$

Thus, after the phase variables are equilibrated at each temperature, the PSN Q-function is locally maximized with respect to the remaining temperature coordinate. This recovers Michelsen's nested PS-flash interpretation [1]. The intermediate chain-rule steps and the thermodynamic identification of $-C_{P,\mathrm{br}}/T$ are given in Appendix E.

5.4. PHN, PTN, and SVN flashes

The remaining cases follow from the same distinction between full and reduced curvature.

For PHN,

$$Q_{\mathrm{PHN}}(T, \boldsymbol{z}_P) = \frac{\overline{A}(T, \boldsymbol{z}_P) + P^{\mathrm{spec}} V - H^{\mathrm{spec}}}{T}. \tag{93}$$

At a stationary point, the first-order conditions cancel the additional quotient-rule terms (see Appendix A), giving

$$\boxed{\nabla^2 Q^\star_{\mathrm{PHN}} = \frac{1}{T^\star}\nabla^2 \overline{A}^\star.} \tag{94}$$

Since $T^\star > 0$, PHN has the same inertia as PSN under the same fixed-temperature stability condition. If $\boldsymbol{K} \succ \boldsymbol{0}$, the reduced outer curvature is

$$\overline{Q}''_{\mathrm{PHN}}(T^\star) = -\frac{C^\star_{P,\mathrm{br}}}{(T^\star)^2} < 0. \tag{95}$$

For the original PHN entropy-maximization problem, equivalently minimization of $-S$, the admissible tangent space is defined by the linearized enthalpy and phase-pressure constraints; Eq. (62) gives the corresponding reduced second-order condition.

For PTN, temperature is specified and is therefore absent from the decision vector. The Q-function is

$$Q_{\mathrm{PTN}}(\boldsymbol{z}_P) = \overline{A}(T^{\mathrm{spec}}, \boldsymbol{z}_P) + P^{\mathrm{spec}} V, \tag{96}$$

and the affine pressure term gives

$$\boxed{\nabla^2_{\boldsymbol{z}_P \boldsymbol{z}_P} Q^\star_{\mathrm{PTN}} = \boldsymbol{K} \succeq \boldsymbol{0}.} \tag{97}$$

Thus the PTN Q-function has nonnegative second-order curvature in its actual Helmholtz-variable decision space, in agreement with Michelsen's volume-based PT formulation [1]. Including T in this Hessian would be incorrect because T is prescribed, not optimized.

For SVN, the total-volume and total-mole balances have already been eliminated, so $\boldsymbol{x}_V = [T, \boldsymbol{z}_V^\top]^\top$ and

$$Q_{\mathrm{SVN}} = \overline{A}(T, \boldsymbol{z}_V) + T S^{\mathrm{spec}}. \tag{98}$$

Again the added term is affine, and therefore $\nabla^2 Q_{\mathrm{SVN}} = \nabla^2 \overline{A}$ in the reduced coordinates. The fixed-temperature block is the projection of the phase Helmholtz Hessians onto perturbations satisfying both total-volume and total-mole balance and is positive semidefinite for locally stable phases. Consequently, the same congruence argument as for PSN gives one negative eigenvalue in the full SVN Q-function Hessian, up to possible zero modes. On the entropy-preserving tangent space, however, the reduced quadratic form is nonnegative at a locally stable constrained internal-energy minimum.

The preceding results are local. Positive semidefiniteness of the relevant reduced Hessian does not establish global phase stability or prove that the globally stable phase assemblage has been found. As in the classical PT flash, a global tangent-plane or equivalent phase-stability test is required to exclude competing phases [1]. Critical, spinodal, invariant-coexistence, and phase-appearance states may introduce zero modes or active inequality constraints and therefore require the corresponding degenerate or critical-cone analysis.

6. Conclusion

Michelsen's Q-functions and their general Legendre-transform construction are established prior results. The contribution of the present work is therefore not the introduction of new Q-functions, but an explicit specification-by-specification derivation and second-order interpretation in Helmholtz-energy variables. By keeping the actual independent-variable spaces and eliminated balances explicit, the derivations show directly how the equilibrium Lagrange-multipliers arise from stationarity and how the Q-function gradients recover the imposed thermodynamic constraints together with mechanical and chemical equilibrium.

The second-order analysis clarifies an important distinction that is obscured if the full Q-function Hessian is interpreted as the stability Hessian of the original flash problem. The full Hessian characterizes the unconstrained saddle geometry of the Q-function, whereas thermodynamic stability of the original constrained minimization is determined by the Hessian projected onto the admissible tangent space. For the Q-functions considered here, these tangent-space quadratic forms coincide with the KKT reduced Hessians of the original constrained problems. Under positive heat capacity and local fixed-temperature Helmholtz stability, the PSN, PHN, and SVN Q-functions possess exactly one negative-curvature direction in the full variable space, apart from possible zero modes, while PTN is locally nonnegative in its actual fixed-temperature decision space. The reduced PSN temperature curvature recovers the familiar $-C_P/T$ result of the nested formulation.

These results are local and do not replace global phase-stability analysis. Degenerate states and active phase-amount constraints require the corresponding critical-cone treatment, while global equilibrium still requires a tangent-plane or equivalent global stability test.

Declaration of Generative AI and AI-assisted technologies in the writing process

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The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Stationary-point simplification of the PHN Q-function Hessian

For the PHN flash, define

$$F(T,\boldsymbol{z}) := \overline{A}(T,\boldsymbol{z}) + P^{\mathrm{spec}}V - H^{\mathrm{spec}}, \qquad Q_{\mathrm{PHN}}(T,\boldsymbol{z}) = \frac{F(T,\boldsymbol{z})}{T}, \tag{A.1}$$

where $\boldsymbol{z}$ contains the independent phase volumes and mole numbers after elimination of the total mole-balance constraints. The first derivatives are

$$Q_T = \frac{F_T}{T} - \frac{F}{T^2}, \qquad \nabla_z Q = \frac{1}{T}\nabla_z F. \tag{A.2}$$

Hence, at a stationary point $(T^\star, \boldsymbol{z}^\star)$,

$$F_T^\star = \frac{F^\star}{T^\star}, \qquad \nabla_z F^\star = \boldsymbol{0}. \tag{A.3}$$

The second derivatives are

$$Q_{TT} = \frac{F_{TT}}{T} - \frac{2F_T}{T^2} + \frac{2F}{T^3}, \tag{A.4}$$

$$\nabla_z Q_T = \frac{1}{T}\nabla_z F_T - \frac{1}{T^2}\nabla_z F, \tag{A.5}$$

$$\nabla^2_{zz} Q = \frac{1}{T}\nabla^2_{zz} F. \tag{A.6}$$

Using (A.3), the additional terms generated by differentiation of $1/T$ cancel or vanish:

$$Q^\star_{TT} = \frac{F^\star_{TT}}{T^\star}, \qquad \nabla_z Q^\star_T = \frac{1}{T^\star}\nabla_z F^\star_T. \tag{A.7}$$

Consequently,

$$\boxed{\nabla^2 Q^\star_{\mathrm{PHN}} = \frac{1}{T^\star}\nabla^2 F^\star = \frac{1}{T^\star}\nabla^2 \overline{A}^\star.} \tag{A.8}$$

The last equality follows because $P^{\mathrm{spec}}V - H^{\mathrm{spec}}$ is affine in the chosen optimization variables and therefore has zero Hessian. Since $T^\star > 0$, multiplication by $1/T^\star$ does not change the inertia of the Hessian. Eq. (A.8) is a stationary-point identity and does not hold in this form away from stationarity.

Appendix B. Relation between the Q-function Hessian and the constrained second variation

Consider the regular equality-constrained optimization problem

$$\min_{\boldsymbol{x}} f(\boldsymbol{x}), \qquad \boldsymbol{c}(\boldsymbol{x}) = \boldsymbol{0}, \tag{B.1}$$

where $\boldsymbol{x} \in \mathbb{R}^n$ denotes the optimization variables and $\boldsymbol{c}(\boldsymbol{x}) \in \mathbb{R}^m$ collects the equality constraints. The corresponding Lagrangian is

$$\mathcal{L}(\boldsymbol{x}, \boldsymbol{\lambda}) = f(\boldsymbol{x}) + \boldsymbol{\lambda}^{\mathsf{T}}\boldsymbol{c}(\boldsymbol{x}). \tag{B.2}$$

Let $(\boldsymbol{x}^\star, \boldsymbol{\lambda}^\star)$ satisfy the KKT conditions.

In the Q-function construction, the equilibrium multipliers are promoted to smooth functions of the thermodynamic variables. Thus,

$$Q(\boldsymbol{x}) = f(\boldsymbol{x}) + \hat{\boldsymbol{\lambda}}(\boldsymbol{x})^{\mathsf{T}}\boldsymbol{c}(\boldsymbol{x}), \qquad \hat{\boldsymbol{\lambda}}(\boldsymbol{x}^\star) = \boldsymbol{\lambda}^\star. \tag{B.3}$$

For example, in the PSN construction, $\hat{\lambda}_S = -T$ and $\hat{\lambda}_P^{(k)} = -V^{(k)}$.

Admissible perturbations

To determine which perturbations are relevant to the original constrained problem, consider a small displacement from the solution,

$$\boldsymbol{x}(\varepsilon) = \boldsymbol{x}^\star + \varepsilon \boldsymbol{d}, \tag{B.4}$$

where ε is a small scalar and $\boldsymbol{d}$ denotes the perturbation direction.

A perturbation is admissible only if it preserves the constraints to first order. Expanding the constraint vector about $\boldsymbol{x}^\star$ gives

$$\boldsymbol{c}(\boldsymbol{x}^\star + \varepsilon\boldsymbol{d}) = \boldsymbol{c}(\boldsymbol{x}^\star) + \varepsilon J_c(\boldsymbol{x}^\star)\boldsymbol{d} + \mathcal{O}(\varepsilon^2), \tag{B.5}$$

where

$$J_c(\boldsymbol{x}^\star) := \left.\frac{\partial \boldsymbol{c}}{\partial \boldsymbol{x}}\right|_{\boldsymbol{x}^\star} \tag{B.6}$$

is the Jacobian of the constraints.

Since $\boldsymbol{x}^\star$ is feasible, $\boldsymbol{c}(\boldsymbol{x}^\star) = \boldsymbol{0}$. Therefore, preservation of the constraints to first order requires

$$\boxed{J_c(\boldsymbol{x}^\star)\boldsymbol{d} = \boldsymbol{0}.} \tag{B.7}$$

Hence the admissible perturbations are precisely the directions in the null space of the constraint Jacobian,

$$\boldsymbol{d} \in \ker J_c(\boldsymbol{x}^\star). \tag{B.8}$$

Geometrically, these directions form the tangent space to the constraint manifold at $\boldsymbol{x}^\star$.

Comparison of the two Hessians

Because $\boldsymbol{c}(\boldsymbol{x}^\star) = \boldsymbol{0}$ and $\hat{\boldsymbol{\lambda}}(\boldsymbol{x}^\star) = \boldsymbol{\lambda}^\star$, the Q-function and the KKT Lagrangian have the same first derivative at the solution,

$$\nabla Q(\boldsymbol{x}^\star) = \nabla_{\boldsymbol{x}}\mathcal{L}(\boldsymbol{x}^\star, \boldsymbol{\lambda}^\star). \tag{B.9}$$

Their full Hessians, however, are generally not identical because $\hat{\boldsymbol{\lambda}}$ depends on $\boldsymbol{x}$. Differentiating (B.3) twice and evaluating at $\boldsymbol{x}^\star$ gives

$$\nabla^2 Q^\star = \nabla^2_{\boldsymbol{xx}}\mathcal{L}^\star + \sum_{i=1}^{m}\left[\nabla\hat{\lambda}_i^\star(\nabla c_i^\star)^{\mathsf{T}} + \nabla c_i^\star(\nabla\hat{\lambda}_i^\star)^{\mathsf{T}}\right]. \tag{B.10}$$

Terms proportional to $c_i(\boldsymbol{x}^\star)$ have vanished because the constraints are satisfied at the solution.

Now consider the second-order curvature along an admissible direction $\boldsymbol{d}$. Premultiplying and postmultiplying (B.10) by $\boldsymbol{d}^{\mathsf{T}}$ and $\boldsymbol{d}$ gives

$$\begin{aligned}\boldsymbol{d}^{\mathsf{T}}\nabla^2 Q^\star \boldsymbol{d} = \boldsymbol{d}^{\mathsf{T}}\nabla^2_{\boldsymbol{xx}}\mathcal{L}^\star\boldsymbol{d} \\ + \sum_{i=1}^{m}\left(\boldsymbol{d}^{\mathsf{T}}\nabla\hat{\lambda}_i^\star\right)\left((\nabla c_i^\star)^{\mathsf{T}}\boldsymbol{d}\right) \\ + \sum_{i=1}^{m}\left(\boldsymbol{d}^{\mathsf{T}}\nabla c_i^\star\right)\left((\nabla\hat{\lambda}_i^\star)^{\mathsf{T}}\boldsymbol{d}\right).\end{aligned} \tag{B.11}$$

The admissibility condition (B.7) implies, for every constraint c_i,

$$(\nabla c_i^\star)^{\mathsf{T}}\boldsymbol{d} = 0. \tag{B.12}$$

Consequently, each of the additional cross terms in (B.11) vanishes. Therefore,

$$\boxed{\boldsymbol{d}^{\mathsf{T}}\nabla^2 Q^\star \boldsymbol{d} = \boldsymbol{d}^{\mathsf{T}}\nabla^2_{\boldsymbol{xx}}\mathcal{L}^\star\boldsymbol{d}, \qquad J_c(\boldsymbol{x}^\star)\boldsymbol{d} = \boldsymbol{0}.} \tag{B.13}$$

Thus, the full Hessians need not be equal, but they produce the same second-order curvature along every admissible perturbation.

Reduced-Hessian form

Let the columns of $\boldsymbol{Z}$ form a basis for the tangent space,

$$\mathrm{Range}(\boldsymbol{Z}) = \ker J_c(\boldsymbol{x}^\star). \tag{B.14}$$

Every admissible perturbation can then be expressed as

$$\boldsymbol{d} = \boldsymbol{Z}\boldsymbol{y}, \tag{B.15}$$

where $\boldsymbol{y}$ contains the coordinates of the perturbation within the tangent space.

Substituting (B.15) into (B.13) gives

$$(\boldsymbol{Z}\boldsymbol{y})^{\mathsf{T}}\nabla^2 Q^\star(\boldsymbol{Z}\boldsymbol{y}) = (\boldsymbol{Z}\boldsymbol{y})^{\mathsf{T}}\nabla^2_{\boldsymbol{xx}}\mathcal{L}^\star(\boldsymbol{Z}\boldsymbol{y}). \tag{B.16}$$

Using $(\boldsymbol{Z}\boldsymbol{y})^{\mathsf{T}} = \boldsymbol{y}^{\mathsf{T}}\boldsymbol{Z}^{\mathsf{T}}$, this becomes

$$\boldsymbol{y}^{\mathsf{T}}\left(\boldsymbol{Z}^{\mathsf{T}}\nabla^2 Q^\star \boldsymbol{Z}\right)\boldsymbol{y} = \boldsymbol{y}^{\mathsf{T}}\left(\boldsymbol{Z}^{\mathsf{T}}\nabla^2_{\boldsymbol{xx}}\mathcal{L}^\star\boldsymbol{Z}\right)\boldsymbol{y}. \tag{B.17}$$

Since (B.17) holds for every tangent-space coordinate vector $\boldsymbol{y}$, the matrices defining the two quadratic forms must be identical. Hence,

$$\boxed{\boldsymbol{Z}^{\top}\nabla^2 Q^{\star}\boldsymbol{Z} = \boldsymbol{Z}^{\top}\nabla^2_{\boldsymbol{xx}}\mathcal{L}^{\star}\boldsymbol{Z}.} \tag{B.18}$$

Eq. (B.18) shows that the Q-function and the original constrained problem have the same reduced Hessian on the physically admissible tangent space. Consequently, a necessary second-order condition for a locally stable constrained solution is

$$\boxed{\boldsymbol{Z}^{\top}\nabla^2 Q^{\star}\boldsymbol{Z} \succeq \boldsymbol{0}.} \tag{B.19}$$

The full Hessian $\nabla^2 Q^{\star}$ may nevertheless be indefinite, because its negative-curvature directions need not satisfy the linearized constraints. Strict positive definiteness of the reduced Hessian gives the standard second-order sufficient condition for a strict local constrained minimum. At phase boundaries, where nonnegativity constraints become active, the tangent space is replaced by the corresponding KKT critical cone.

Appendix C. Role of the quadratic form in the second-order analysis

Let $\boldsymbol{H} = \nabla^2 Q(\boldsymbol{x}^{\star})$ denote the Hessian of a Q-function at a stationary point $\boldsymbol{x}^{\star}$. Consider a small perturbation

$$\boldsymbol{x}(\varepsilon) = \boldsymbol{x}^{\star} + \varepsilon\boldsymbol{d}, \tag{C.1}$$

where $\boldsymbol{d}$ specifies the perturbation direction. A Taylor expansion gives

$$Q(\boldsymbol{x}^{\star} + \varepsilon\boldsymbol{d}) = Q(\boldsymbol{x}^{\star}) + \varepsilon\nabla Q(\boldsymbol{x}^{\star})^{\top}\boldsymbol{d} + \frac{\varepsilon^2}{2}\boldsymbol{d}^{\top}\boldsymbol{H}\boldsymbol{d} + \mathcal{O}(\varepsilon^3). \tag{C.2}$$

Since $\boldsymbol{x}^{\star}$ is stationary, $\nabla Q(\boldsymbol{x}^{\star}) = \boldsymbol{0}$, and therefore the leading change is governed by the quadratic form

$$\boxed{\boldsymbol{d}^{\top}\boldsymbol{H}\boldsymbol{d}.} \tag{C.3}$$

Its sign determines the local second-order curvature in the direction $\boldsymbol{d}$: it is positive for upward curvature, negative for downward curvature, and zero for a locally flat direction.

For an unconstrained problem, all perturbation directions are admissible. Thus,

$$\boldsymbol{H} \succeq \boldsymbol{0} \iff \boldsymbol{d}^{\top}\boldsymbol{H}\boldsymbol{d} \geq 0 \quad \text{for all } \boldsymbol{d}. \tag{C.4}$$

For a constrained flash problem, however, only perturbations satisfying the linearized constraints are physically admissible. If $\boldsymbol{Z}$ spans the corresponding tangent space, every admissible perturbation can be written as

$$\boldsymbol{d} = \boldsymbol{Z}\boldsymbol{y}. \tag{C.5}$$

The quadratic form then becomes

$$\boldsymbol{d}^{\top}\boldsymbol{H}\boldsymbol{d} = \boldsymbol{y}^{\top}\left(\boldsymbol{Z}^{\top}\boldsymbol{H}\boldsymbol{Z}\right)\boldsymbol{y}. \tag{C.6}$$

Hence the relevant curvature for constrained stability is governed by the reduced Hessian

$$\boxed{\boldsymbol{Z}^{\top}\boldsymbol{H}\boldsymbol{Z},} \tag{C.7}$$

rather than by the sign of the full Hessian in directions that may violate the flash constraints. This explains how a Q-function may be saddle-shaped in the unrestricted variable space while retaining nonnegative curvature along all physically admissible perturbations.

Appendix D. Sylvester's law of inertia

For completeness, we recall the form of Sylvester's law of inertia used in the Hessian analysis. Let $\boldsymbol{H} \in \mathbb{R}^{n\times n}$ be symmetric and let $\boldsymbol{R}$ be any nonsingular matrix. The matrices

$$\boldsymbol{H} \quad \text{and} \quad \boldsymbol{R}^{\top}\boldsymbol{H}\boldsymbol{R} \tag{D.1}$$

are said to be *congruent*. Sylvester's law of inertia states that congruent real symmetric matrices have the same numbers of positive, negative, and zero eigenvalues. Thus,

$$\mathrm{In}(\boldsymbol{H}) = \mathrm{In}(\boldsymbol{R}^{\top}\boldsymbol{H}\boldsymbol{R}), \qquad \mathrm{In}(\boldsymbol{H}) := (n_+, n_-, n_0), \tag{D.2}$$

where n_+, n_-, and n_0 denote the numbers of positive, negative, and zero eigenvalues, respectively.

This result is useful because a symmetric block matrix can often be simplified by a congruence transformation without explicitly calculating its eigenvalues. For example, for

$$\boldsymbol{H} = \begin{bmatrix} a & \boldsymbol{g}^{\top} \\ \boldsymbol{g} & \boldsymbol{K} \end{bmatrix}, \qquad a \neq 0, \tag{D.3}$$

a suitable nonsingular transformation gives

$$\boldsymbol{H} \sim \begin{bmatrix} a & \boldsymbol{0}^{\top} \\ \boldsymbol{0} & \boldsymbol{K} - \frac{1}{a}\boldsymbol{g}\boldsymbol{g}^{\top} \end{bmatrix}, \tag{D.4}$$

where "$\sim$" denotes congruence. Consequently, the inertia of $\boldsymbol{H}$ is obtained directly from the signs of a and of the eigenvalues of its Schur-complement block

$$\boldsymbol{K} - \frac{1}{a}\boldsymbol{g}\boldsymbol{g}^{\top}. \tag{D.5}$$

In particular, if $a < 0$ and $\boldsymbol{K} \succeq \boldsymbol{0}$, then

$$\boldsymbol{K} - \frac{1}{a}\boldsymbol{g}\boldsymbol{g}^{\top} = \boldsymbol{K} + \frac{1}{|a|}\boldsymbol{g}\boldsymbol{g}^{\top} \succeq \boldsymbol{0}. \tag{D.6}$$

Hence the original matrix has exactly one negative eigenvalue, apart from any possible zero modes in the lower block. This is the form of Sylvester's law used in the PSN and related Q-function Hessian analyses.

Appendix E. Reduced temperature curvature of the PSN Q-function

This appendix gives the intermediate steps leading to the reduced temperature curvature of the PSN Q-function. The purpose is to distinguish the curvature obtained when all Q-function variables are varied independently from that obtained after the phase variables have been equilibrated at each temperature.

For the PSN specification,

$$Q_{\mathrm{PSN}}(T, \boldsymbol{z}_P) = \overline{A}(T, \boldsymbol{z}_P) + P^{\mathrm{spec}}V + TS^{\mathrm{spec}}, \tag{E.1}$$

where $\boldsymbol{z}_P$ collects the independent phase volumes and mole numbers after elimination of the total mole balances. At fixed P^{spec} and $\boldsymbol{N}^{\mathrm{spec}}$, consider a local phase-equilibrium branch

$$\boldsymbol{z}_P = \overline{\boldsymbol{z}}_P(T) \tag{E.2}$$

defined implicitly by

$$\nabla_{z_P} Q_{\mathrm{PSN}}\left(T, \overline{\boldsymbol{z}}_P(T)\right) = \boldsymbol{0}. \tag{E.3}$$

Thus, for each nearby value of T, the phase variables are allowed to readjust so that mechanical and chemical equilibrium are maintained. If

$$\boldsymbol{K} := \nabla^2_{z_P z_P} Q_{\mathrm{PSN}} = \nabla^2_{z_P z_P}\overline{A} \tag{E.4}$$

is nonsingular, the implicit-function theorem ensures that $\overline{\boldsymbol{z}}_P(T)$ is locally smooth.

Variation of the equilibrium phase variables with temperature

Differentiate (E.3) with respect to T. Because the gradient depends on T both directly and through $\overline{\boldsymbol{z}}_P(T)$, the chain rule gives

$$\boldsymbol{0} = \frac{\mathrm{d}}{\mathrm{d}T}\nabla_{z_P} Q_{\mathrm{PSN}}\left(T, \overline{\boldsymbol{z}}_P(T)\right)$$

$$= \nabla^2_{z_P T} Q_{\mathrm{PSN}} + \nabla^2_{z_P z_P} Q_{\mathrm{PSN}} \frac{\mathrm{d}\overline{\boldsymbol{z}}_P}{\mathrm{d}T}. \tag{E.5}$$

Introducing

$$\boldsymbol{g} := \nabla^2_{z_P T} Q_{\mathrm{PSN}} = \nabla_{z_P} \overline{A}_T, \tag{E.6}$$

we obtain

$$\boldsymbol{g} + \boldsymbol{K} \frac{\mathrm{d}\overline{\boldsymbol{z}}_P}{\mathrm{d}T} = \boldsymbol{0}. \tag{E.7}$$

Hence, when $\boldsymbol{K}$ is invertible,

$$\boxed{\frac{\mathrm{d}\overline{\boldsymbol{z}}_P}{\mathrm{d}T} = -\boldsymbol{K}^{-1}\boldsymbol{g}.} \tag{E.8}$$

Eq. (E.8) describes how the equilibrium phase volumes and compositions respond to a small change in temperature at fixed P^{spec} and $\boldsymbol{N}^{\mathrm{spec}}$.

Reduction of the Q-function to the temperature coordinate

Define the Q-function restricted to this phase-equilibrium branch by

$$\overline{Q}_{\mathrm{PSN}}(T) := Q_{\mathrm{PSN}}\left(T, \overline{\boldsymbol{z}}_P(T)\right). \tag{E.9}$$

The first derivative follows from the chain rule:

$$\frac{\mathrm{d}\overline{Q}_{\mathrm{PSN}}}{\mathrm{d}T} = Q_T + \left(\nabla_{z_P} Q_{\mathrm{PSN}}\right)^{\mathsf{T}} \frac{\mathrm{d}\overline{\boldsymbol{z}}_P}{\mathrm{d}T}. \tag{E.10}$$

Along the branch, $\nabla_{z_P} Q_{\mathrm{PSN}} = \boldsymbol{0}$, and therefore

$$\boxed{\overline{Q}'_{\mathrm{PSN}}(T) = Q_T.} \tag{E.11}$$

Using $\overline{A}_T = -S$ in (E.1),

$$Q_T = -S + S^{\mathrm{spec}}, \tag{E.12}$$

so that

$$\boxed{\overline{Q}'_{\mathrm{PSN}}(T) = S^{\mathrm{spec}} - S_{\mathrm{br}}(T),} \tag{E.13}$$

where $S_{\mathrm{br}}(T)$ denotes the entropy of the state on the local phase-equilibrium branch. The PSN solution $T^\star$ is therefore the point on this branch at which

$$S_{\mathrm{br}}(T^\star) = S^{\mathrm{spec}}. \tag{E.14}$$

Differentiating (E.11) once more gives

$$\overline{Q}''_{\mathrm{PSN}}(T) = Q_{TT} + Q_{T z_P} \frac{\mathrm{d}\overline{\boldsymbol{z}}_P}{\mathrm{d}T}. \tag{E.15}$$

With

$$a := Q_{TT} = \overline{A}_{TT}, \qquad Q_{T z_P} = \boldsymbol{g}^{\mathsf{T}}, \tag{E.16}$$

Eq. (E.15) becomes

$$\overline{Q}''_{\mathrm{PSN}} = a + \boldsymbol{g}^{\mathsf{T}} \frac{\mathrm{d}\overline{\boldsymbol{z}}_P}{\mathrm{d}T}. \tag{E.17}$$

Substituting (E.8) then yields

$$\boxed{\overline{Q}''_{\mathrm{PSN}}(T^\star) = a - \boldsymbol{g}^{\mathsf{T}} \boldsymbol{K}^{-1} \boldsymbol{g}.} \tag{E.18}$$

Since

$$a = \overline{A}^\star_{TT} = -\frac{C^\star_{V,\mathrm{tot}}}{T^\star}, \tag{E.19}$$

the first term represents the temperature curvature obtained when the phase variables are held fixed. The second term accounts for the additional change arising because the phase volumes and compositions readjust as temperature varies.

Connection with the equilibrium heat capacity

Along the fixed-P^{spec}, fixed-$\boldsymbol{N}^{\mathrm{spec}}$ phase-equilibrium branch,

$$\overline{A}\left(T, \overline{\boldsymbol{z}}_P(T)\right) + P^{\mathrm{spec}} V = G_{\mathrm{br}}\left(T, P^{\mathrm{spec}}, \boldsymbol{N}^{\mathrm{spec}}\right), \tag{E.20}$$

where G_{br} denotes the Gibbs energy of the local equilibrium branch. Hence

$$\overline{Q}_{\mathrm{PSN}}(T) = G_{\mathrm{br}}\left(T, P^{\mathrm{spec}}, \boldsymbol{N}^{\mathrm{spec}}\right) + T S^{\mathrm{spec}}. \tag{E.21}$$

If the branch corresponds to the globally stable phase state, G_{br} may be identified with the equilibrium Gibbs energy.

At fixed pressure and total mole numbers,

$$\left(\frac{\partial G_{\mathrm{br}}}{\partial T}\right)_{P,\boldsymbol{N}} = -S_{\mathrm{br}}, \tag{E.22}$$

and therefore differentiation of (E.21) again gives

$$\overline{Q}''_{\mathrm{PSN}} = -\left(\frac{\partial S_{\mathrm{br}}}{\partial T}\right)_{P,\boldsymbol{N}}. \tag{E.23}$$

Defining the heat capacity along this equilibrium branch by

$$C_{P,\mathrm{br}} := T\left(\frac{\partial S_{\mathrm{br}}}{\partial T}\right)_{P,\boldsymbol{N}}, \tag{E.24}$$

we obtain

$$\boxed{\overline{Q}''_{\mathrm{PSN}}(T^\star) = -\frac{C^\star_{P,\mathrm{br}}}{T^\star}.} \tag{E.25}$$

For a stable branch with $C^\star_{P,\mathrm{br}} > 0$, the reduced Q-function therefore has negative temperature curvature.

Finally, comparing (E.18) and (E.25) with $a = -C^\star_{V,\mathrm{tot}}/T^\star$ gives

$$-\frac{C^\star_{P,\mathrm{br}}}{T^\star} = -\frac{C^\star_{V,\mathrm{tot}}}{T^\star} - \boldsymbol{g}^{\mathsf{T}} \boldsymbol{K}^{-1} \boldsymbol{g}, \tag{E.26}$$

or equivalently

$$\boxed{C^\star_{P,\mathrm{br}} = C^\star_{V,\mathrm{tot}} + T^\star \boldsymbol{g}^{\mathsf{T}} \boldsymbol{K}^{-1} \boldsymbol{g}.} \tag{E.27}$$

Thus, after the phase variables are equilibrated at each temperature, the multivariable PSN Q-function reduces locally to a one-dimensional function of T. Its stationary condition enforces the specified entropy, while its negative second derivative, $-C_{P,\mathrm{br}}/T$, explains the temperature maximization appearing in the nested PS-flash interpretation.

Appendix F. Calculus identities

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \left[\left(\frac{\partial Y}{\partial X}\right)_Z\right]^{-1} \tag{F.1}$$

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \left(\frac{\partial X}{\partial W}\right)_Z \left(\frac{\partial W}{\partial Y}\right)_Z \tag{F.2}$$

$$\left(\frac{\partial X}{\partial Y}\right)_Z = -\left(\frac{\partial Z}{\partial Y}\right)_X \Big/ \left(\frac{\partial Z}{\partial X}\right)_Y \tag{F.3}$$

$$\left(\frac{\partial Z}{\partial Y}\right)_W = \left(\frac{\partial Z}{\partial Y}\right)_X + \left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_W \tag{F.4}$$

Thermodynamic identities:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{F.5}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{F.6}$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{F.7}$$

$$\left(\frac{\partial A}{\partial P}\right)_T = -P\left(\frac{\partial V}{\partial P}\right)_T \tag{F.8}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \tag{F.9}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \tag{F.10}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{F.11}$$

Data availability

No data was used for the research described in the article.

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