

Canonical Form and Mathematical Interpretation of Electrolyte Solution Systems

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Abstract—We describe a canonical form of electrolyte solution systems for the mathematical interpretation of solid-liquid equilibrium. The canonical form is obtained from the analysis of the algebraic structure of electrolyte solution systems and the Karush-Kuhn-Tucker (KKT) conditions for the minimization of the total Gibbs free energy. As a result, the mathematical role of solid species in the solid-liquid equilibrium problem is explained as a Lagrange multiplier of a sort of the linearly constrained optimization problem. This finding will add to the development of an efficient numerical algorithm for the simulation of electrolyte solution systems.

Key words: Electrolyte Solution, Canonical Form, Solid-Liquid Equilibrium, Lagrange Multiplier, Inorganic Aerosol

INTRODUCTION

Chemical processes related to electrolyte solutions involving precipitated solid phases represent an important aspect of modern chemical engineering, in areas such as inorganic fine chemicals, pharmaceuticals, and environmental protection [Hong, 2003]. In these processes, electrolytes in the aqueous solution dissociate completely or partly into corresponding ions, and solid phases are often precipitated depending on the process condition. For process simulation, one must predict whether a given feed will be split into multiple phases, the number of phases and their identities, and the distribution of species within these phases. The same requirements are also charged to accurately assess the role that aerosols play in atmospheric phenomena. Atmospheric aerosols have a direct impact on earth's radiation balance, fog formation and cloud physics, and visibility degradation as well as human health effect [Martin, 2000]. Of central importance to these effects is the hygroscopic nature of the atmospheric aerosols in moist air. Historically, hygroscopic properties of aerosols have been attributed to the inorganic fraction.

One of the most challenging parts for electrolyte solution systems is the prediction of the partitioning of the inorganic components between aqueous and solid phases. A direct minimization of the Gibbs free energy implicitly predicts phase evolution without any *a priori* knowledge of the behavior of electrolyte solution. However, the direct minimization approach disregards the specific mathematical structure of the solid-liquid equilibrium problem. As a result, it is computationally intensive to be used in large-scale applications. For an equation-based approach, provided that the set of mass balance and equilibrium relations can be determined algorithmically to reflect the actual state of electrolyte system under the varying process condition, its solution corresponds to the minimum of the Gibbs free energy and thus predicts the physical state of electrolyte systems correctly. To attack this problem, we present a canonical form of electrolyte solution systems and then give the mathematical inter-

pretation of solid-liquid equilibrium stage. The canonical framework reported here for examples of inorganic aerosols is general and then of great utility for developing an efficient numerical algorithm for predicting the phase evolution of electrolyte solution systems.

ALGEBRAIC STRUCTURE OF ELECTROLYTE SOLUTION SYSTEMS

In this section, the canonical forms of the mass balance and the chemical equilibrium relations are systematically derived to develop a basis for the equation-based approach handling solid-liquid equilibrium rationally.

1. Canonical Stoichiometry

An essential first step is to identify all the chemicals expected to be present in the system. All these chemicals are referred to *species*. Consider a *closed* electrolyte solution system of n species χ_1, \dots, χ_n , whose molecular structures are described by the *formula matrix* $\hat{\mathbf{A}}_{pm} = (\hat{\mathbf{a}}_1, \dots, \hat{\mathbf{a}}_n)$ defined by

$$\chi_j = \sum_{i=1}^m \hat{a}_{ij} \epsilon_i, \quad \text{for } j=1, \dots, n.$$

The species are constituted as the linear combination of the m *basic elements*, $\epsilon_1, \dots, \epsilon_m$ (note that the electronic charge is also a basic element). Let \mathcal{I}_{pm} be the index set of the chemical species with $n = |\mathcal{I}_{pm}|$ as the number of species. The index set \mathcal{I}_{pm} can be split into \mathcal{I}_l and \mathcal{I}_s with $n_l = |\mathcal{I}_l|$ and $n_s = |\mathcal{I}_s|$ according to the aqueous and solid phases, respectively. The formula matrices of both phases are defined by:

$$\hat{\mathbf{A}}_l = (\hat{\mathbf{a}}_i)_{i \in \mathcal{I}_l} \quad \text{and} \quad \hat{\mathbf{A}}_s = (\hat{\mathbf{a}}_i)_{i \in \mathcal{I}_s}.$$

One very efficient formulation for the computation of electrolyte thermodynamic equilibrium is based on *Tableau concept* [Morel and Morgan, 1972]. A smaller set of chemicals characterizing the system is defined as *components*. Specifically, the components in a system are defined as a set of chemicals that satisfies the following two criteria: (1) combinations of the components can be used to generate all the species in the system, and (2) none of the components can be generated solely by a combination of other components. It is clear that no individual chemical entity is inherently ac-

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^{*}This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

ceptable or unacceptable as a component, and that the components can only be acceptable or unacceptable as a complete set. Also, the set of components is not unique and any system can be represented by one of the possible sets of components. In electrolyte solution systems, the aqueous species formula matrix $\hat{\mathbf{A}}_l \in \mathbb{R}^{m \times n_l}$ is assumed to have full row rank. Let $\mathcal{I}_c (\subset \mathcal{I}_l)$ be a set of $m (=|\mathcal{I}_c|)$ aqueous species whose corresponding formula vectors $\hat{\mathbf{a}}_i$ are linearly independent (i.e., $\hat{\mathbf{A}}_c^{-1}$ exists) - these are the components; let $\mathcal{I}_n = \mathcal{I}_l - \mathcal{I}_c$ be the set of the remaining $n_l - m (=|\mathcal{I}_n|)$ aqueous species with the formula matrix $\hat{\mathbf{A}}_n = (\hat{\mathbf{a}}_i)_{i \in \mathcal{I}_n}$. These are called the non-component species.

Once the species have been identified and a set of components chosen, there is only one way to write the reaction forming each species from the chosen components with the unique equilibrium constant, and the stoichiometry for each species is uniquely defined. The information relating the species to the components can be summarized in a concise matrix with each column containing the stoichiometric coefficients and the equilibrium constant for forming a particular species from the chosen components. Let

$$\mathbf{A}_\pi = (a_{ij}^\pi) = \hat{\mathbf{A}}_c^{-1} \hat{\mathbf{A}}_\pi, \quad \text{for } \pi = \text{pm}, l, c, n, s, \quad (1)$$

be the *component-based* formula matrix; these are also called the *canonical stoichiometric matrix* associated with the chemical equilibrium reactions in the canonical form.

Denoted by \mathbf{x}_π , for $\pi = \text{pm}, l, c, n, s$, the concentration vector of each category of species. A schematic diagram of a solid-liquid equilibrium (SLE) stage in electrolyte solution is shown in Fig. 1. Here the mass balance of an SLE stage is given by:

$$\mathbf{x}_c + \mathbf{A}_n \mathbf{x}_n + \mathbf{A}_s \mathbf{x}_s = \mathbf{b}_c \quad (2)$$

where $\mathbf{b}_c \in \mathbb{R}^m$ is a given component-based feed vector.

2. Canonical Equilibrium Relation

The determination of the equilibrium distribution in a closed system at constant temperature and pressure is a minimization problem:

$$\min_{\bar{\mathcal{I}}_s, \mathbf{x}_{\text{pm}}} G(\mathbf{x}_{\text{pm}}; \mathbf{b}_c) \quad (3)$$

subject to the mass balance (2), $\mathbf{x}_l > \mathbf{0}$ and $\mathbf{x}_s \geq \mathbf{0}$, where the total Gibbs free energy G is given by:

$$G = \mu_c^T \mathbf{x}_c + \mu_n^T \mathbf{x}_n + \mu_s^T \mathbf{x}_s \quad (4)$$

and $\mu_\pi = (\mu_{\pi,i})_{i \in \mathcal{I}_\pi}$, for $\pi = c, n, s$, is the chemical potential vector for the species set π . The set of the solid species is further divided into $\bar{\mathcal{I}}_s = \{i \in \mathcal{I}_s: x_{s,i} > 0\}$ and $\bar{\mathcal{I}}_s = \{i \in \mathcal{I}_s: x_{s,i} = 0\}$. The set of the solid species actually formed, $\bar{\mathcal{I}}_s$, is *a priori* unknown and is determined by the minimization. The first order necessary conditions for a minimum G (i.e., Karush-Kuhn-Tucker conditions in the canonical stoichiometric form) are:

$$\mathbf{x}_c + \mathbf{A}_n \mathbf{x}_n + \mathbf{A}_s \mathbf{x}_s = \mathbf{b}_c$$

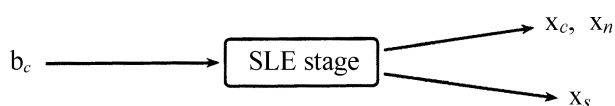


Fig. 1. Schematic diagram of a Solid-Liquid Equilibrium stage in electrolyte solution: \mathbf{x}_π , for $\pi = c, n, s$, is the concentration vector of components, non-components, and solid species, respectively and \mathbf{b}_c is the component-based feed vector.

$$\begin{aligned} \mu_n - \mathbf{A}_n^T \mu_c &= \mathbf{0} \\ \mu_s - \mathbf{A}_s^T \mu_c &\geq \mathbf{0} \\ \mathbf{x}_s &\geq \mathbf{0} \\ \mathbf{x}_s^T (\mu_s - \mathbf{A}_s^T \mu_c) &= \mathbf{0}. \end{aligned} \quad (5)$$

The chemical potential of each category of species is given by the expression:

$$\mu_\pi = \mu_\pi^o + RT \ln a_\pi \quad (6)$$

where μ_π^o is the standard chemical potential vector at 1 atm and temperature T and a_π denotes the activity vector.

Let

$$-RT \ln \mathbf{k}_\pi = \mathbf{A}_\pi^T \mu_c^o - \mu_\pi^o \quad (7)$$

be the equilibrium constant vector associated with the canonical stoichiometry. After substituting the Eqs. (6) and (7) into the Eq. (5) and rearranging, the KKT conditions are transformed into the mass action laws with the mass balance constraint. The distribution of species in the aqueous phase is governed by the following canonical speciation equilibrium reactions:

$$\chi_i \xleftrightarrow{k_{n,i}} \sum_{j \in \mathcal{I}_c} a_{ij} \chi_j, \quad \forall i \in \mathcal{I}_n$$

and the mass action law is written with the canonical speciation constant vector \mathbf{k}_n and the canonical stoichiometric \mathbf{A}_n matrix:

$$\ln a_n = \mathbf{A}_n^T \ln a_c - \ln \mathbf{k}_n \quad (8)$$

We have the mass action law in a logarithmic form here. An immediate consequence of the logarithmic form is that the mass action law has a linear functional relation. Once the equilibrium constants and stoichiometry for forming the non-component species from the components are established, specifying the activities of all the components allows one to compute the corresponding equilibrium activities of all the species. The precipitation of salts is controlled by the canonical solid-liquid equilibrium reactions as follows:

$$\chi_k \xleftrightarrow{k_{s,k}} \sum_{j \in \mathcal{I}_s} s_{jk} \chi_j, \quad \forall k \in \bar{\mathcal{I}}_s$$

and the mass action law is then given by using the canonical precipitation constant vector \mathbf{k}_s and the canonical stoichiometric matrix \mathbf{A}_s :

$$\ln s_p = \mathbf{A}_s^T \ln a_c - \ln \mathbf{k}_s \quad (9)$$

in which

$$s_{p,k} = 1, \quad \text{for } k \in \bar{\mathcal{I}}_s \quad \text{and} \quad s_{p,k} < 1, \quad \text{for } k \in \bar{\mathcal{I}}_s. \quad (10)$$

3. Example: Typical Urban Aerosols

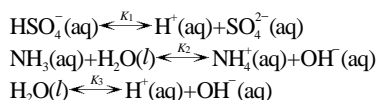
The predominant inorganic components of atmospheric aerosols in the 1 μm size range and smaller are ammonium, nitrate, and sulfate. Ammonia is present in virtually all terrestrial air masses and condenses on aerosol particles where it neutralizes aerosol acidity. Nitric acid is formed by gas phase oxidation of primary NO_x emissions and moves to the aerosol phase to equilibrate the gas and aerosol phases. Sulfate is formed by gas phase oxidation of SO_2 and is transported to the aerosol phase, where it remains due to its low vapor pressure.

In case of the typical urban aerosol [Pandis et al., 1995], the chemicals expected to be present in the aqueous phase include H_2O , H^+ ,

Table 1. Canonical stoichiometric matrix A_n and canonical speciation equilibrium constant vector k_n of the typical urban aerosol

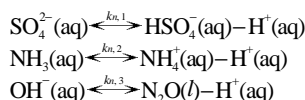
	H ₂ O	H ⁺	HSO ₄ ⁻	NO ₃ ⁻	NH ₄ ⁺	
Species	$A_n^T = (a_{ji}^n)$					k_n
SO ₄ ²⁻	0	-1	1	0	0	$k_{n,1} = 1/K_1$
NH ₃	0	-1	0	0	1	$k_{n,2} = K_2/K_3$
OH ⁻	1	-1	0	0	0	$k_{n,3} = 1/K_3$

HSO₄⁻, SO₄²⁻, NO₃⁻, NH₃, NH₄⁺, and OH⁻ and three speciation equilibrium reactions can be considered:



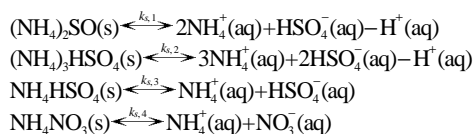
where basic elements are H, O, N, S, and electronic charge.

Say we chose as *components* H₂O, H⁺, HSO₄⁻, NO₃⁻, and NH₄⁺. Five of the species are chemically identical to corresponding components, so obviously those species are formed from the components directly. The remaining three species (SO₄²⁻, NH₃, and OH⁻) can be generated by appropriate combinations of the components as follows:



where $k_{n,1} = 1/K_1$, $k_{n,2} = K_2/K_3$, and $k_{n,3} = 1/K_3$. Table 1 shows a canonical stoichiometric matrix A_n and canonical speciation equilibrium constant vector k_n obtained from the above arguments.

If a solid phase exists in the aerosol, then it represents a separate phase whose activity is fixed. The rules for defining the stoichiometry of the solid species are identical to those for forming the aqueous species, and the precipitation constant $k_{s,k}$ is simply obtained from the solubility product $K_{p,k}$ of the solid species and $k_{n,i}$'s. For the typical urban aerosol, the possible species for the solid phase are (NH₄)₂SO₄, (NH₄)₃H(SO₄)₂, NH₄HSO₄ and NH₄NO₃. The canonical solid-liquid equilibrium reactions are as follows:



where $k_{s,1} = K_{p,1}/k_{n,1}$, $k_{s,2} = K_{p,2}/k_{n,1}$, $k_{s,3} = K_{p,3}$, and $k_{s,4} = K_{p,4}$. Table 2 shows canonical stoichiometric matrix A_s and canonical precipita-

Table 2. Canonical stoichiometric matrix A_s and canonical precipitation constant vector k_s of the typical urban aerosol

	H ₂ O	H ⁺	HSO ₄ ⁻	NO ₃ ⁻	NH ₄ ⁺	
Solid species	$A_s^T = (a_{ji}^s)$					k_s
(NH ₄) ₂ SO ₄	0	-1	1	0	2	$k_{s,1} = K_{p,1}/k_{n,1}$
(NH ₄) ₃ H(SO ₄) ₂	0	-1	2	0	3	$k_{s,2} = K_{p,2}/k_{n,1}$
NH ₄ HSO ₄	0	0	1	0	1	$k_{s,3} = K_{p,3}$
NH ₄ NO ₃	0	0	0	1	1	$k_{s,4} = K_{p,4}$

tion constant vector k_s of the solid phases of the typical urban aerosol based on the same set of components as Table 1.

4. Number of Solid Phases and Their Identities

An electrolyte solution has n_c independent components: it is the minimum number of chemicals that can be used to generate all the chemical species present at equilibrium. According to the *Gibbs phase rule*, a chemical system has $n_c - \pi + 2$ degrees of freedom, in which π is the number of phases in equilibrium. In almost all systems of interest, the temperature and total pressure of the system are assumed to be known. Furthermore, since we are always interested in the aqueous solution that contains dissolved electrolytes, the charge balance places another constraint on the system. Therefore, the system of interest always has at least three pre-specified constraints, so the largest possible number of solid phases in equilibrium with an aqueous phase is $\sup|\bar{I}_s| = n_c - 2$. Also, it may be impossible for any set of all the possible solid species to coexist with the aqueous solution. As a physical constraint, \bar{I}_s is an index set of the solid species corresponding to the linearly-independent columns of A_s . For instance, (NH₄)₂SO₄, (NH₄)₃H(SO₄)₂, and NH₄HSO₄ cannot exist simultaneously. If (NH₄)₂SO₄ and (NH₄)₃H(SO₄)₂ coexist in an aerosol particle, the following condition is satisfied:

$$a_{\text{NH}_4^+} a_{\text{HSO}_4^-} = \frac{k_{s,(\text{NH}_4)_2\text{SO}_4}}{k_{s,(\text{NH}_4)_3\text{H}(\text{SO}_4)_2}}$$

and thus

$$s_{p,\text{NH}_4\text{HSO}_4} = \frac{k_{s,(\text{NH}_4)_2\text{SO}_4}}{k_{s,(\text{NH}_4)_3\text{H}(\text{SO}_4)_2} k_{s,\text{NH}_4\text{HSO}_4}} < 1.$$

That is, NH₄HSO₄ cannot coexist with two other solids in a single aerosol particle. Fig. 2 shows the conceivable configurations of solid-liquid equilibrium in the typical urban aerosol.

At present, the number of solid phases $\bar{n}_s = |\bar{I}_s|$ and their identities \bar{I}_s are determined in advance by using phase diagrams or an enumerative method. The former method used in the most of the equation-based models is unsuitable for complicated systems and infeasible to calculate continuously. In the latter method, all combinations should be tried, and good initial values are often required to calculate the activity coefficients of liquid components reliably. The computational burden and the difficulty of estimating initial values limit the use of this method in practice. Another method based on free energy minimization implicitly predicts the number of phases and their identities through nonlinear programming. However, nonlinear programming for a direct minimization of the free energy is

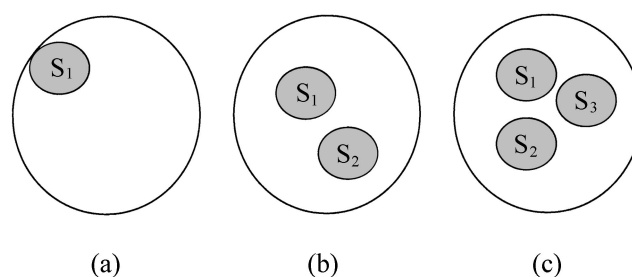


Fig. 2. Conceivable configurations of SLE stages in the typical urban aerosol: (a) $\bar{I}_s = \{1\}, \{2\}, \{3\}$, and $\{4\}$, (b) $\bar{I}_s = \{1, 2\}, \{2, 3\}, \{1, 4\}$, and $\{2, 4\}$, (c) $\bar{I}_s = \{1, 2, 4\}$ and $\{2, 3, 4\}$, (1: (NH₄)₂SO₄, 2: (NH₄)₃H(SO₄)₂, 3: NH₄HSO₄, 4: NH₄NO₃).

computationally intensive, making its use in large-scale process simulation unreliable.

MATHEMATICAL ROLE OF SOLID SPECIES IN AN SLE STAGE

Here a mathematical role of solid species in solid-liquid equilibrium is exploited to identify the number of phases and their identities rationally. We work on the following additional notation:

$$\begin{aligned}\bar{\mathbf{x}} &= \ln(\mathbf{x}_c^T \quad \mathbf{x}_n^T)^T \\ \lambda &= \mathbf{x}_s \\ \mathbf{y} &= \ln(a_c^T \quad a_n^T)^T \\ \xi &= \ln a_s \\ \mathbf{b}_n &= -\ln \mathbf{k}_n \\ \mathbf{b}_s &= -\ln \mathbf{k}_s \\ \mathbf{T} &= (\mathbf{I}_c \quad \mathbf{A}_n)^T \\ \mathbf{A}_\lambda &= -\mathbf{A}_s^T\end{aligned}$$

in which $\bar{\mathbf{x}} \in \mathbb{R}^{n_l}$. Then the mass balance has the corresponding form:

$$\mathbf{T}^T \exp(\bar{\mathbf{x}}) - \mathbf{A}_\lambda^T \lambda = \mathbf{b}_c \quad (11)$$

In turn, the mass action laws for the distribution of the aqueous species and the solid precipitation are written by:

$$-\mathbf{T} \xi + \mathbf{y}(\bar{\mathbf{x}}) = \begin{pmatrix} \mathbf{0} \\ \mathbf{b}_n \end{pmatrix} \quad (12)$$

and

$$\begin{aligned}\mathbf{A}_\lambda \xi - \mathbf{b}_\lambda &\geq 0 \\ \lambda &\geq \mathbf{0} \\ \lambda^T (\mathbf{A}_\lambda \xi - \mathbf{b}_\lambda) &= 0.\end{aligned} \quad (13)$$

This mass balance and mass action laws of variational inequality type can be viewed as a *Karush-Kuhn-Tucker* system. Consider the following linearly constrained optimization problem:

$$\min_{\xi} f(\xi) \quad \text{subject to} \quad \mathbf{A}_\lambda \xi \geq \mathbf{b}_\lambda \quad (14)$$

where f is a smooth function. We say that $\xi^* \in \mathbb{R}^{n_c}$ is a local solution of (14) if

- it is feasible for (14) - that is, $\mathbf{A}_\lambda \xi^* \geq \mathbf{b}_\lambda$;
- there is a scalar $\rho > 0$ such that $f(\xi) \geq f(\xi^*)$ for all feasible $\|\xi - \xi^*\| < \rho$.

The first-order necessary conditions for the optimality, also known as the *Karush-Kuhn-Tucker* conditions, are given in the following theorem.

Theorem 1 Suppose that ξ^* is a local solution of (14) and that is differentiable in a neighborhood of ξ^* . Then there is a vector λ such that the following conditions hold:

$$\begin{aligned}\nabla_{\xi} f(\xi^*) - \mathbf{A}_\lambda^T \lambda &= \mathbf{0} \\ \mathbf{A}_\lambda \xi^* &\geq \mathbf{b}_\lambda \\ \lambda &\geq \mathbf{0} \\ \lambda^T (\mathbf{A}_\lambda \xi^* - \mathbf{b}_\lambda) &= 0\end{aligned}$$

The vector λ is a *Lagrange multiplier*. For a proof, see Fletcher,

[1987].

As a result, we observe that an SLE stage problem can be viewed as the *KKT* conditions of the linearly constrained optimization problem (14) that satisfy the following equations:

$$\begin{aligned}\nabla_{\xi} f(\bar{\mathbf{x}}) &= \mathbf{T}^T \exp(\bar{\mathbf{x}}) - \mathbf{b}_c \\ \mathbf{h}(\xi, \bar{\mathbf{x}}) &= \mathbf{T} \xi - \mathbf{y}(\bar{\mathbf{x}}) + \begin{pmatrix} \mathbf{0} \\ \mathbf{b}_n \end{pmatrix} = \mathbf{0}\end{aligned}$$

and then the mathematical role of solid species in an SLE stage is a Lagrange multiplier λ associated to the linear inequality constraints.

Recent literature on the numerical optimization for the linearly constrained problem can be divided into two main classes. On the one hand, there are “active-set” approaches. In these algorithms a model of f (for example, the quadratic approximation) is formed at each “outer” iteration and minimized over some subset of the feasible region. The algorithm tends to move along edges and faces of the boundary of the feasible set, changing the set of currently active constraints by at most one element on each “inner” iteration. A second class of methods, known as “gradient projection” methods, allow more substantial changes to the active set at each iteration by choosing a direction g (for example, ∇f or some scaled version of it) and searching along the piecewise linear path $P(\xi - \alpha g)$, where $\alpha > 0$ and P is the projection onto the feasible set. The optimization techniques mentioned can give the rational method determining the number of phases and their identities automatically through the equation-based approach.

CONCLUSIONS

In this work, our purpose was to investigate the computational framework providing the set of mass balance and equilibrium relations reflecting the actual state of the electrolyte system under the varying process condition. From the canonical formulation of electrolyte solution systems, we realized the mathematical role of solid species in solid-liquid equilibrium as a Lagrange multiplier of a sort of the linearly constrained optimization problem. This observation naturally links the solid-liquid equilibrium problem to optimization techniques such as active-set approaches and gradient projection methods in order to identify the number of phases and their identities in the equation-based approach.

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