# General Optimality Criteria for Multiphase Multireaction Chemical Equilibrium

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This note presents a new formulation of the most general case of multiphase, multireaction (*chemical*) equilibrium, and two new global chemical equilibrium criteria arising from it. This formulation involves the new concept of a *phase class* (as defined below), which allows the most general case in which every substance need not occur in every phase of the system (as in the important case where pure condensed phases are present in addition to multispecies phases). This is coupled with a particular choice of variables for each phase class in the problem formulation.

The two new criteria resulting from this formulation are:

(1) A *necessary and sufficient* condition that must be satisfied by all feasible phase compositions *and* amounts at the global minimum of the Gibbs function ($G$),

(2) A supporting hyperplane criterion for each phase class, which is also a *necessary and sufficient* condition that must be satisfied by all phase *compositions* for each phase class at such a global minimum.

Note that our development shows that the tangent plane criterion used for *phase equilibrium* (Baker et al., 1982; Michelsen, 1982a) is a special case of our second criterion above for *chemical equilibrium*.

The movitation for this work lies in the difficulties that arise in computing equilibrium in a multiphase, multireaction system, as the number of possible phases increases, especially for nonideal systems. The difficulties include:

- Intrinsic difficulties relating to nonuniqueness, that is, the mathematical presence of local minima and maxima in the $G$ surface, which in turn relate to distinguishing among thermodynamically stable, metastable and unstable equilibrium states
- Lack of *a priori* criteria for determining the number of possible phases that can be described by a given chemical potential ("free energy") model, which is related to the case of an assumed phase of given composition "splitting" into one, or more than one, other phase described by the same free energy model
- Numerical difficulties as described, for example, by Smith and Missen (1988, 1991).

Other workers (Zeleznik and Gordon, 1968; Gautam and Seider, 1979a,b; Michelsen, 1982a,b; Harvie et al., 1987; Paules and Floudas, 1989; Gupta et al., 1990, 1991) have been concerned with various aspects of the general problem, the approach of Harvie et al. and of Gupta et al. being closest in philosophy to ours.

## New Formulation of Chemical Equilibrium Problem

We consider a chemical system at specified temperature, $T$, and pressure, $P$, so that $G$ is the appropriate thermodynamic potential function to be considered for optimality, with the following assumed to be given:

- A substance formula matrix, $A_s \in E^{M\times S}$, where $M$ is the number of elements and $S$ is the number of substances, each of which is distinguished by a formula vector $\boldsymbol{a}_i$ which is a column of $A_s$; we assume here that rank $(A_s) < S$ and is usually given by $M$
- An elemental-abundance vector, $\boldsymbol{b} \in E^M$, with entries $b_j \geq 0$ and $\boldsymbol{b} \neq \boldsymbol{0}$
- A set of $\pi$ *phase classes* characterized by the chemical potential models $\{\mu^\beta(T,P,x^\beta,\alpha^\beta);\ \beta = 1, 2, \ldots, \pi\}$:

where

| | | |
|---|---|---|
| $\mu^\beta$ | : | $E^{2+I^\beta+\tilde{\alpha}^\beta} \rightarrow E^{I^\beta}$ |
| $x^\beta \in E^{I^\beta}$ | = | composition (mole-fraction) vector for $\mu^\beta$ |
| $\alpha^\beta \in E^{\alpha^\beta}$ | = | vector of model parameters for $\mu^\beta$ |
| $\tilde{I}^\beta$ | = | cardinality of the index set $I^\beta$ for the substances deemed to be accessible to any phase consistent with the phase class $\beta$ |
| $\tilde{\alpha}^\beta$ | = | number of chemical potential model parameters given by $\alpha^\beta$ |

We assume that each phase class satisfies the Gibbs-Duhem equation, as well as the limiting law $\lim_{x_i^\beta \to 0} \mu_i^\beta = -\infty$. Note that $\cup_{\beta=1}^{\pi} I^\beta = \{1, 2, \ldots, S\}$, that is, every substance in the

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system is accessible to (occurs in) at least one phase class; furthermore, all substances need not be accessible to every phase class. The number of phase classes, $\pi$, is specified *a priori*; $\pi^\beta$, the number of phases consistent with phase class $\beta$, is not known *a priori*; and $\pi$ and $\pi^\beta$ are distinct from the total number of phases present at equilibrium in nonzero amounts, $\Pi$, which is also not known *a priori*, but is one of the results of the equilibrium computation. For phase $k$ consistent with phase class $\beta$, we have $\mu^{\beta,k} = \mu^\beta(T, P, x^{\beta,k}, \alpha^\beta)$, where $x^{\beta,k} \epsilon E^{I^\beta}$ is the composition vector for this phase.

The general statement of the chemical equilibrium problem at specified $T$, $P$, and $b$ is given by (omitting the dependence of $\mu^\beta$ on $T$, $P$, $\alpha^\beta$):

$$\min_{\tilde{n}^{\beta,k},\ x^{\beta,k}} G = \sum_{\beta=1}^{\pi} \sum_{k=1}^{\pi^\beta} \tilde{n}^{\beta,k} \sum_{i \epsilon I^\beta} x_i^{\beta,k} \mu_i^\beta(x^{\beta,k}) \tag{1}$$

subject to:

$$\tilde{n}^{\beta,k} \geq 0; \quad \beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{2}$$

$$x_i^{\beta,k} \geq 0; \quad i \epsilon I^\beta, \quad \beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{3}$$

$$\sum_{\beta=1}^{\pi} \sum_{k=1}^{\pi^\beta} \tilde{n}^{\beta,k} \sum_{i \epsilon I^\beta} a_{ji} x_i^{\beta,k} - b_j = 0; \quad j = 1, 2, \ldots, M \tag{4}$$

$$\sum_{i \epsilon I^\beta} x_i^{\beta,k} - 1 = 0; \quad \beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{5}$$

where $\tilde{n}^{\beta,k}$ is the total number of moles in phase $\beta,k$. In all cases, we assume that at least one feasible solution exists.

In the case of *phase* equilibrium alone, the problem statement is given by Eqs. 1-3 and 5, with the element balance (Eq. 4) now replaced by the substance balance:

$$\sum_{\beta=1}^{\pi} \sum_{k=1}^{\pi^\beta} \tilde{n}^{\beta,k} x_i^{\beta,k} - q_i = 0; \quad i = 1, 2, \ldots, S \tag{6}$$

where $q_i (\geq 0)$ is the (constant) total number of moles of substance $i$ in the system.

This formulation can be contrasted with earlier work (for example, that by Zeleznik and Gordon, 1968), in that we have incorporated the nonnegativity constraints explicitly from the outset. Inequality constraints are most appropriately treated by the techniques of modern optimization theory (see, for example, Bazaraa and Shetty, 1979). The chemical equilibrium problem, however, has a special mathematical structure, the consequences of which have not been elaborated by these techniques. The equilibrium criteria which follow are examples of such consequences.

## Kuhn-Tucker Conditions

Noting that the constraint qualification that the gradient vectors of the binding constraints are linearly independent (Bazaraa and Shetty, 1979, p. 137) is satisfied, we may write the first-order Kuhn-Tucker necessary conditions (Bazaraa and Shetty, 1979, p. 146) for the general form of the equilibrium problem represented in relations 1-5 as:

$$\nabla \left( \sum_{\beta=1}^{\pi} \sum_{k=1}^{\pi^\beta} \tilde{n}^{\beta,k} \sum_{i \epsilon I^\beta} x_i^{\beta,k} \mu_i^\beta(x^{\beta,k}) \right) - \sum_{\beta=1}^{\pi} \sum_{k=1}^{\pi^\beta} \theta^{\beta,k} \nabla(\tilde{n}^{\beta,k})$$
$$- \sum_{\beta=1}^{\pi} \sum_{k=1}^{\pi^\beta} \sum_{i \epsilon I^\beta} \omega_i^{\beta,k} \nabla(x_i^{\beta,k}) - \sum_{j=1}^{M} \lambda_j \nabla \left( \sum_{\beta=1}^{\pi} \sum_{k=1}^{\pi^\beta} \tilde{n}^{\beta,k} \sum_{i \epsilon I^\beta} a_{ji} x_i^{\beta,k} - b_j \right)$$
$$- \sum_{\beta=1}^{\pi} \sum_{k=1}^{\pi^\beta} \rho^{\beta^k} \nabla \left( \sum_{i \epsilon I^\beta} x_i^{\beta,k} - 1 \right) = \mathbf{0} \tag{7}$$

where $\nabla$ is the gradient vector with respect to the variables $\{x^{\beta,k}, \tilde{n}^{\beta,k}\}$, and $\theta^{\beta,k}$, $\omega_i^{\beta,k}$, $\lambda_j$ and $\rho^{\beta,k}$ are Lagrange multipliers, associated with constraints 2, 3, 4 and 5, respectively, together with:

*The complementary slackness conditions*:

$$\theta^{\beta,k} \tilde{n}^{\beta,k} = 0; \quad \beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{8}$$

$$\omega_i^{\beta,k} x_i^{\beta,k} = 0; \quad i \epsilon I^\beta, \quad \beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{9}$$

*The nonnegativity constraints*:

$$\theta^{\beta,k} \geq 0; \quad \beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{10}$$

$$\omega_i^{\beta,k} \geq 0; \quad i \epsilon I^\beta, \quad \beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{11}$$

*The equality constraints of Eqs. 4 and 5.*

Evaluation of Eq. 7 and incorporation of the Gibbs-Duhem equation for each phase in the system yield the pair of equations:

$$\tilde{n}^{\beta,k} \mu_i^\beta(x^{\beta,k}) - \omega_i^{\beta,k} - \tilde{n}^{\beta,k} \sum_{j=1}^{M} \lambda_j a_{ji} - \rho^{\beta,k} = 0;$$
$$i \epsilon I^\beta, \quad \beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{12}$$

$$\sum_{i \epsilon I^\beta} x_i^{\beta,k} \mu_i^\beta(x^{\beta,k}) - \theta^{\beta,k} - \sum_{j=1}^{M} \lambda_j \sum_{i \epsilon I^\beta} a_{ji} x_i^{\beta,k} = 0;$$
$$\beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{13}$$

Thus, the equilibrium criteria which result from the first-order Kuhn-Tucker conditions are given by relations 4, 5 and 8-13.

The Lagrange multipliers $\rho^{\beta,k}$ and $\omega_i^{\beta,k}$ may be shown to vanish as follows. From Eqs. 13 and 8:

$$\theta^{\beta,k} \tilde{n}^{\beta,k} = \tilde{n}^{\beta,k} \sum_{i \epsilon I^\beta} x_i^{\beta,k} \left( \mu_i^\beta(x^{\beta,k}) - \sum_{j=1}^{M} \lambda_j a_{ji} \right) = 0;$$
$$\beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{14}$$

Multiplying Eq. 12 by $x_i^{\beta,k}$, using Eq. 9 and summing the result over $i \epsilon I^\beta$, we have:

$$\sum_{i \epsilon I^\beta} \omega_i^{\beta,k} x_i^{\beta,k} = \tilde{n}^{\beta,k} \sum_{i \epsilon I^\beta} x_i^{\beta,k} \left( \mu_i^\beta(x^{\beta,k}) - \sum_{j=1}^{M} \lambda_j a_{ji} \right)$$
$$- \rho^{\beta,k} \sum_{i \epsilon I^\beta} x_i^{\beta,k} = 0; \quad \beta = 1, 2, \ldots, \pi, \quad k = 1, 2, \ldots, \pi^\beta \tag{15}$$

Equations 14 and 15, along with Eq. 5, give:

$$\rho^{\beta,k}=0;\ \ \beta=1,\ 2,\ \ldots,\ \pi,\ \ k=1,\ 2,\ \ldots,\ \pi^{\beta} \tag{16}$$

From Eqs. 12 and 16, we have:

$$\omega_i^{\beta,k}=\tilde{n}^{\beta,k}\left(\mu_i^{\beta}(x^{\beta,k})-\sum_{j=1}^{M}\lambda_j a_{ji}\right)=0;$$

$$i\in I^{\beta},\ \ \beta=1,\ 2,\ \ldots,\ \pi,\ \ k=1,\ 2,\ \ldots,\ \pi^{\beta} \tag{17}$$

From Eq. 17, if for any phase $\beta$, $k$, $\tilde{n}^{\beta,k}=0$, then $\omega_i^{\beta,k}=0$ for all $i\in I^{\beta}$. Also, if $\tilde{n}^{\beta,k}>0$ then $x_i^{\beta,k}>0$ for all $i\in I^{\beta}$ (Smith and Missen, 1991, p. 57) and hence from Eq. 9, in general:

$$\omega_i^{\beta,k}=0;\ \ i\in I^{\beta},\ \ \beta=1,\ 2,\ \ldots,\ \pi,\ \ k=1,\ 2,\ \ldots,\ \pi^{\beta} \tag{18}$$

The relations which govern the equilibrium are thus:

$$\tilde{n}^{\beta,k}\left(\mu_i^{\beta}(x^{\beta,k})-\sum_{j=1}^{M}\lambda_j a_{ji}\right)=0;\ \ i\in I^{\beta},$$

$$\beta=1,\ 2,\ \ldots,\ \pi,\ \ k=1,\ 2,\ \ldots,\ \pi^{\beta} \tag{19}$$

$$\theta^{\beta,k}=\sum_{i\in I^{\beta}}x_i^{\beta,k}\left(\mu_i^{\beta}(x^{\beta,k})-\sum_{j=1}^{M}\lambda_j a_{ji}\right)\geq 0;$$

$$\beta=1,\ 2,\ \ldots,\ \pi,\ \ k=1,\ 2,\ \ldots,\ \pi^{\beta} \tag{20}$$

$$\theta^{\beta,k}\tilde{n}^{\beta,k}=0;\ \ \beta=1,\ 2,\ \ldots,\ \pi,\ \ k=1,\ 2,\ \ldots,\ \pi^{\beta} \tag{8}$$

$$\sum_{\beta=1}^{\pi}\sum_{k=1}^{\pi^{\beta}}\tilde{n}^{\beta,k}\sum_{i\in I^{\beta}}a_{ji}x_i^{\beta,k}-b_j=0;\ \ j=1,\ 2,\ \ldots,\ M \tag{4}$$

$$\sum_{i\in I^{\beta}}x_i^{\beta,k}-1=0;\ \ \beta=1,\ 2,\ \ldots,\ \pi,\ \ k=1,\ 2,\ \ldots,\ \pi^{\beta} \tag{5}$$

We call a solution $(\{\tilde{n}^{\beta,k},\ x^{\beta,k}\},\ \lambda,\ \theta)$ of Eqs. 19, 20, 8, 4 and 5 a Kuhn-Tucker (KT) point.

## Global Optimality Conditions: Two New Criteria

Global optimality conditions ensure that a KT point gives the *global* minimum of the system Gibbs function. At such a point, Eqs. 8 and 20 give:

$$\tilde{n}^{\beta,k}\sum_{i\in I^{\beta}}x_i^{\beta,k}\left(\mu_i^{\beta}(x^{\beta,k})-\sum_{j=1}^{M}\lambda_j a_{ji}\right)=0;$$

$$\beta=1,\ 2,\ \ldots,\ \pi,\ \ k=1,\ 2,\ \ldots,\ \pi^{\beta} \tag{21}$$

Summing over $k$ and $\beta$, and rearranging, we obtain:

$$G^{\dagger}=\sum_{\beta=1}^{\pi}\sum_{k=1}^{\pi^{\beta}}\tilde{n}^{\beta,k}\sum_{i\in I^{\beta}}x_i^{\beta,k}\mu_i^{\beta}(x^{\beta,k})=\sum_{\beta=1}^{\pi}\sum_{k=1}^{\pi^{\beta}}\tilde{n}^{\beta,k}\sum_{i\in I^{\beta}}x_i^{\beta,k}\sum_{j=1}^{M}\lambda_j^{\dagger}a_{ji}$$

$$=\sum_{j=1}^{M}\lambda_j^{\dagger}b_j \tag{22}$$

where we have used $^{\dagger}$ to emphasize that the quantity refers to the KT point. $G^{\dagger}$ is the Gibbs function at the KT point, and the last equality follows from Eq. 4.

A KT point is globally optimal if, and only if, the value of its Gibbs function does not exceed that given by *any* feasible set of $\{\tilde{n}^{\beta,k},\ x^{\beta,k}\}$. We may express this as:

$$\sum_{\beta=1}^{\pi}\sum_{k=1}^{\pi^{\beta}}\tilde{n}^{\beta,k}\sum_{i\in I^{\beta}}x_i^{\beta,k}\mu_i^{\beta}(x^{\beta,k})\geq G^{\dagger} \tag{23}$$

Using Eqs. 4 and 22, we may write this as:

$$\Delta G^{\dagger}=\sum_{\beta=1}^{\pi}\sum_{k=1}^{\pi^{\beta}}\tilde{n}^{\beta,k}\sum_{i\in I^{\beta}}x_i^{\beta,k}\left(\mu_i^{\beta}(x^{\beta,k})-\sum_{j=1}^{M}\lambda_j^{\dagger}a_{ji}\right)\geq 0 \tag{24}$$

for all $\{\tilde{n}^{\beta,k},\ x^{\beta,k}\}$ satisfying Eqs. 2-5.

In the case $\pi=1$, criterion 24 becomes, for reaction *and* phase equilibrium:

$$\sum_{k=1}^{\pi^1}\tilde{n}^{k}\sum_{i=1}^{S}x_i^{k}\left(\mu_i^{k}(x^{k})-\sum_{j=1}^{M}\lambda_j^{\dagger}a_{ji}\right)\geq 0 \tag{25}$$

for all $\{\tilde{n}^{k},\ x^{k}\}$ satisfying Eqs. 2-5. (In this case, $I^1=\{1,\ 2,\ \ldots,\ S\}$, and for simplicity, we have suppressed the index $\beta$ except in $\pi^{\beta}$.)

For *phase equilibrium*, criterion 24 becomes:

$$\sum_{\beta=1}^{\pi}\sum_{k=1}^{\pi^{\beta}}\tilde{n}^{\beta,k}\sum_{i\in I^{\beta}}x_i^{\beta,k}(\mu_i^{\beta}(x^{\beta,k})-\mu_i^{\dagger})\geq 0 \tag{26}$$

for all $\{\tilde{n}^{k},\ x^{k}\}$ satisfying Eqs. 2, 3, 5 and 6, where $\mu_i^{\dagger}$ is the value of the chemical potential at the KT point.

Relation 24 is the most general form of the first criterion referred to at the outset above, and relations 25 and 26 are special forms as indicated. All three are both *necessary and sufficient* criteria for global optimality. We are in the process of constructing an algorithm for the numerical implementation of criterion 24 and its special forms.

Relation 24 involves both the total numbers of moles in all phases and the mole fractions in each phase as the variable set. We may obtain a simpler set of conditions involving only the mole fraction variables for each phase class from the inner summation in relation 24:

$$\sum_{i\in I^{\beta}}x_i\left(\mu_i^{\beta}(x)-\sum_{j=1}^{M}\lambda_j^{\dagger}a_{ji}\right)\geq 0;\ \ \beta=1,\ 2,\ \ldots,\ \pi \tag{27}$$

for all nonnegative $x$ satisfying Eq. 5. This is the most general form of the second criterion referred to at the outset above. The *sufficiency* of relation 27 follows directly from consideration in conjunction with relation 24, since its satisfaction implies satisfaction of relation 24. The proof of relation 27 as a *necessary* condition is lengthy and difficult, and is treated elsewhere (Ye et al., 1993).

We note the superficial similarity of relation 27 to relation 20. However, the latter applies only to a KT point and is a *local* criterion; the former, on the other hand, is a *global* criterion.

The reasons for introducing criterion 27 are twofold: it should be useful as an "inner part" of an algorithm for implementing criterion 24, and it also represents the generalization to chemical reaction of a commonly used criterion for phase equilibrium.

Thus for the latter, the case of phase equilibrium, a *necessary and sufficient* condition for a KT point to be globally optimal, from criterion 27, is that:

$$\sum_{i \in I^{\beta}} x_i(\mu_i^{\beta}(\boldsymbol{x}) - \mu_i^{\dagger}) \geq 0; \quad \beta = 1, 2, \ldots, \pi \tag{28}$$

for all nonnegative $\boldsymbol{x}$ satisfying Eq. 5.

Criterion 28 for the case $\pi = 1$ is usually referred to as the *tangent-plane* criterion (cf. Baker et al., 1982; Appendix; Michelsen, 1982a, relation 5), and relation 27 is its generalization to the case of reactions. The tangent hyperplane to the molar Gibbs $[g(\boldsymbol{x})]$ surface is given by the second term in each of the above criteria, and $g(\boldsymbol{x})$ is given by the first term. The criteria state that $g(\boldsymbol{x})$ must lie everywhere above its tangent hyperplanes, or equivalently, that a tangent hyperplane at a KT point must be a *supporting* hyperplane.

## Conclusions

A new formulation of the general chemical equilibrium problem, Eqs. 1-5, is given. Arising from this, relations 24 and 27 are two new criteria for global chemical equilibrium. The tangent-plane criterion of phase equilibrium is a special case of relation 27. We plan to develop a numerical implementation of these criteria to improve the efficiency of computation of chemical equilibrium in multiphase, multireaction systems.


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## Notation

$\boldsymbol{a}_i$ = formula vector of substance $i$; entry $j$ is $a_{ji}$
$a_{ji}$ = subscript of the $j$th element in the molecular formula of substance $i$
$A_s$ = substance formula matrix; $A_s = (\boldsymbol{a}_1, \boldsymbol{a}_2, \ldots, \boldsymbol{a}_i, \ldots, \boldsymbol{a}_s)$
$\boldsymbol{b}$ = elemental abundance vector with entries $b_j$
$b_j$ = number of moles of element $j$
$E$ = Euclidian space
$g$ = molar Gibbs function
$G$ = Gibbs function
$\Delta G^{\dagger}$ = difference between $G$ at any feasible point and $G$ at KT point
$I^{\beta}$ = index set of all substances accessible to phase class $\beta$
$\tilde{I}^{\beta}$ = cardinality of index set $I^{\beta}$
KT = Kuhn-Tucker (point)
$M$ = number of elements
$\tilde{n}$ = total number of moles
$P$ = pressure
$q_i$ = number of moles of substance $i$
$S$ = number of substances
$T$ = temperature
$\boldsymbol{x}$ = composition (mole fraction) vector with entries $x_i$
$x_i$ = mole fraction of substance $i$

### *Greek letters*

$\boldsymbol{\alpha}^{\beta}$ = vector of model parameters for $\mu^{\beta}$
$\tilde{\alpha}^{\beta}$ = number of chemical potential model parameters given by $\boldsymbol{\alpha}^{\beta}$
$\theta$ = Lagrange multiplier associated with constraint relation 2
$\lambda$ = Lagrange multiplier associated with constraint Eq. 4
$\mu_i$ = chemical potential of substance $i$
$\mu^{\beta}$ = chemical potential model for phase class $\beta$
$\pi$ = number of chemical potential models or phase classes
$\pi^{\beta}$ = number of phases consistent with phase class $\beta$
$\Pi$ = total number of phases present in nonzero amounts at equilibrium
$\rho$ = Lagrange multiplier associated with constraint Eq. 5
$\omega$ = Lagrange multiplier associated with constraint relation 3

### *Superscripts*

$k$ = phase index
$\beta$ = phase class index
$\dagger$ = function value at KT point

### *Subscripts*

$i, j, k$ = dummy indexes

### *Others*

$\in$ = is a member of
$\cup$ = union
$\nabla$ = gradient vector with respect to the variables $\{\boldsymbol{x}^{\beta,k}, \tilde{n}^{\beta,k}\}$
$\{\ \}$ = a set of

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