

## Reaction rates as virtual constraints in Gibbs energy minimization\*

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**Abstract:** The constrained Gibbs energy method has been developed for the use of immaterial entities in the formula conservation matrix of the Gibbs energy minimization problem. The new method enables the association of the conservation matrix with structural, physical, chemical, and energetic properties, and thus the scope of free energy calculations can be extended beyond the conventional studies of global chemical equilibria and phase diagrams. The use of immaterial constraints enables thermochemical calculations in partial equilibrium systems as well as in systems controlled by work factors. In addition, they allow the introduction of mechanistic reaction kinetics to the Gibbsian multiphase analysis. The constrained advancements of reactions are incorporated into the Gibbs energy calculation by using additional virtual phases in the conservation matrix. The virtual components are then utilized to meet the incremental consumption of reactants or the formation of products in the kinetically slow reactions. The respective thermodynamic properties for the intermediate states can be used in reaction rate formulations, e.g., by applying the reaction quotients.

**Keywords:** constrained Gibbs energy minimization; reaction quotients; reaction rates; virtual components; virtual species.

### INTRODUCTION

The formulation of irreversible chemical–thermodynamic systems far from equilibrium has been developed over a period of several decades. The early target of such work was to deduce relations between thermodynamic standard-state quantities and activation energy [1] and to connect the generic reaction rate expressions with the thermodynamic affinity concept [1,2]. In the extensive work of J. Ross and his co-workers, it was shown that the net reaction rate can be combined with the thermodynamic affinity, and thus with the activities of a non-ideal system while the assumption of the local thermodynamic equilibrium is valid [3,4]. This condition suggests that irrespective of a given concentration of chemical species in the reacting system at a given time, the thermodynamic intensive variables such as temperature remain defined. Consequently, the chemical potential may be deduced for each species during the course of such chemical change. As there are a large number of interesting phenomena in chemistry, physics, and biology well within this assumption, it is of interest to have a method, by which the chemical potential can be followed in a complex thermodynamic system during an arbitrary chemical change.

Chemical potentials are conventionally used as the basis of complex equilibrium calculations and phase diagram studies [5,6]. For complex systems with a large number of phases and chemical con-

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stituents, the Gibbs free energy minimization, subject to mass balance constraints of the thermodynamic system, is often used. A comprehensive treatment of the methods used in both chemical reaction and phase equilibrium analysis has been given in a book by Smith and Missen [7], whereas, e.g., Eriksson has developed efficient and multipurpose computational techniques for the use of the equilibrium approach [8]. For methods used in chemical engineering, see, e.g., McDonald and Floudas [9] and the review article by Seider and Widagdo [10]. The methods generally allow the consideration of metastable phases as well as conservation of stoichiometric degrees of freedom in the minimization routines.

A few approaches to combine reaction kinetics with Gibbs energy minimization have also been published. Keck and Gillespie [11,12] presented the rate-controlled constrained equilibrium (RCCE) method for use in fuel combustion calculations. In order to overcome the problem of determining all kinetic parameters, the approach simplifies a set of ordinary differential equations for reaction rates by dividing them into slow and fast reactions. All fast reactions are assumed to reach equilibrium, while all other reactions proceed according to their rate expressions. The equations are integrated so that the time-evolution can be simulated and the solution is used as a set of “passive constraints” in the Gibbs energy calculation. This technique has since been applied in the domain of combustion problems [13]. A related topic is the employing of differential equations to model the dynamic mass balances in process simulation. For example, the approach of Pérez-Cisneros and Gani [14,15] uses the material conservation matrix as input, but the numerical task involves only differential constraints derived from it (see also Blomberg and Koukkari [16]).

Introduction of global reaction rates as constraints to the Gibbsian calculation was suggested by Koukkari [17,18]. The Ratemix method by Koukkari and Niemelä [19] describes a Gibbsian algorithm, which can be used for reaction systems far from equilibrium. The use of reaction rates as constraints was then refined to a more general approach by Pajarre and Koukkari [20–22] in the constrained free energy (CFE) method. One of the immaterial constraints introduced in the new method is the extent of chemical reaction, which then allows for the direct calculation of affinities during a chemical change in a complex system. In what follows, we show that the method is also consistent with the disciplines of thermodynamic equilibrium analysis and can be efficiently used for systems far from equilibrium under the assumptions of the local chemical equilibrium (LCE).

## THE GIBBS ENERGY MINIMIZATION PROBLEM WITH INEQUALITY CONSTRAINTS

Convex minimization with nonlinear objective function and linear constraints is one of the fundamental problems in thermodynamics. When the temperature and pressure are assumed known, the Gibbs energy is the appropriate function to be minimized. It is calculated as the sum of all molar Gibbs energies, multiplied by the respective molar amounts. The sum contains all constituents, whether they are chemical species in different phases, organic isomer groups [23], transformed biochemical metabolites [24], or virtual phases [20]. The objective function is nonlinear because the chemical potentials are functions of the molar amounts. The mathematical expressions for the chemical potentials (molar Gibbs energies) depend largely on the phase models used. In terms of the chemical potentials of the constituents, the Gibbs energy is as follows:

$$G = \sum_k^N n_k \mu_k \quad (1)$$

where  $n_k$  is the molar amount of constituent  $k$ ,  $\mu_k$  is the molar Gibbs energy of constituent  $k$ , and  $N$  is the number of constituents.

The minimization of the Gibbs energy function is subject to linear constraints, which are due to the conservation of components forming the constituents.

$$\min G(\mathbf{n}) \text{ s.t. } \mathbf{C}^T \mathbf{n} = \mathbf{b} ; n_k \geq 0 \quad \forall k \quad (2)$$

where  $\mathbf{C}$  is the component conservation matrix,  $\mathbf{n}$  is the molar amount vector for the constituents, and  $\mathbf{b}$  is the molar amount vector for the components.

The global minimum represents the equilibrium state with the lowest energy reachable with the given set of constraints. The constraints typically refer to elemental amounts of a closed system, but may include conservation of various other components [20]. The solution may also be referred to as a constrained equilibrium or “virtual state” (without the word “equilibrium”) if constraints of dynamic character have been used [12,20].

In both cases, the solution of eq. 2 is obtained by using the method of Lagrange multipliers. The chemical potential of each species is a stoichiometric linear combination of the (equilibrium) potentials of the independent components [7,8,20]

$$\mu_k = \sum_j^{NC} c_{kj} \pi_j \quad (3)$$

where  $\pi_j$  is the Lagrange multiplier corresponding to entity constraint  $j$ ,  $NC$  is the total number of components in the system,  $c_{kj}$  is the (stoichiometric) element of the conservation matrix  $\mathbf{C}$ .

The Gibbs energy of the entire system is, respectively

$$G = \sum_k^N (\mu_k^\circ + RT \ln a_k) n_k = \sum_j^{NC} b_j \pi_j \quad (4)$$

where  $a_k$  denotes the activity of the species  $k$  and  $b_j$  is the conserved amount of each component  $j$ ;  $\mu_k^\circ$  is the chemical potential of the species as a pure phase in the given temperature and pressure. In both equations, the equilibrium potential of the components is denoted by  $\pi_j$ .

The physical meaning of the Lagrange multipliers is that they represent how much potential energy a component contributes to the molar Gibbs energy of a constituent. Thus, if immaterial entities are used as components, their contribution becomes included as an additional term in the chemical potential of each constituent. Keck has introduced the term “constraint potential” to these additional factors appearing the RCCE method [12].

The physically reasonable solution of constituent amounts requires that all  $n_k$  receive a non-negative value. This condition incorporates the inequality conditions

$$\mu_k^\circ - \sum_j^{NC} c_{kj} \pi_j = 0; \quad \forall k ; n_k > 0 \quad (5)$$

$$\mu_k^\circ - \sum_j^{NC} c_{kj} \pi_j > 0; \quad \forall k ; n_k = 0 \quad (6)$$

Together with eq. 2, the conditions 5 and 6 represent the KKT (Karush–Kuhn–Tucker) conditions for the Gibbs energy minimization problem [7]. The latter have here been written for pure invariant phases. For mixture phases the approach is more complex, yet the above expressions are completely sufficient for the use of these inequality conditions in setting kinetic constraints for the minimization algorithm.

As was stated above, a number of computer codes exist, which perform the Gibbs energy minimization. Many of these have not been developed for merely academic purposes, but as well for use in industrial simulations. The most widespread application is for generating phase diagrams of complex systems, but the Gibbsian technique has also been increasingly adapted for process simulation purposes. Of the many programs available, in this work we mainly refer to the properties of the subroutine ChemApp [25], which in addition to performing the  $\min(G)$  task, also provides the thermodynamic

properties of the complex system with a flexible programmable interface and allows for the modifications of one's calculation system. The latter feature is most important, when the immaterial constraints necessary for rate-controlled calculations are applied.

## SYSTEMS CONTROLLED BY REACTION RATES

Reaction rates, or, alternatively, extents of reaction can be included in the  $\min(G)$  calculation by extending the conservation matrix by a particular immaterial component connected with the advancement of a given reaction. To use this feature merely as a passive constraint, a new immaterial component may be included for any given reactant or product. By adapting the technique of virtual invariant phases, both forward and reverse reactions may be considered and the subsequent calculation steps can be performed through the entire range of the extent of reaction. The chemical change is then also calculated by the minimization algorithm itself, and thus the respective changes in the thermodynamic properties are inherently taken into account within the thermodynamic procedure.

The details of using the immaterial components together with virtual invariant phases to control the extent of forward or reverse reactions in Gibbs energy minimization have been described earlier [26,27]. When chemical reactions are constrained by using the virtual components, the following relations can be deduced from the Gibbsian system for the equilibrium reactions and restricted non-equilibrium reactions as follows:

$$\sum_k \nu_k \mu_k = 0 \text{ (equilibrium reactions)} \quad (7)$$

$$\sum_k \nu_k \mu_k = \sum_k \left( \nu_k \sum_{j=NC'+1}^{NC} c_{kj} \pi_j \right) \neq 0 \text{ (all constrained non-equilibrium reactions)} \quad (8)$$

In eqs. 7 and 8,  $\nu_k$  is used for the stoichiometric coefficient of species  $k$  in a given reaction and the respective summation is over the reactants and products. The summation of the Lagrange multipliers ( $\pi_j$ ) in eq. 8 goes over all the virtual components in the system, for which then  $j > NC'$  as  $NC'$  has been used for the number of physical components. It is obvious that through the latter equation the calculated potentials on the virtual components ("constraint potentials") are related to the *affinity* of the non-equilibrium reactions. The affinity ( $A$ ) is defined as [1,4,28]

$$A = -\sum_k \nu_k \mu_k = RT \ln \left( K_{\text{eq}} \prod_k a_k^{-\nu_k} \right) = -\sum_k \left( \nu_k \sum_{j=NC'+1}^{NC} c_{kj} \pi_j \right) \quad (9)$$

Here,  $a_k$  relates to the thermodynamic activity of a given constituent and  $K_{\text{eq}}$  is the activity-based equilibrium coefficient of a given reaction. Formulation of the reaction rate of a elementary reaction in terms of the activities was presented by Haase [1] as follows:

$$r = k \prod_{\text{reactants}} (a_k)^{|\nu_k|} \left[ 1 - e^{-A/RT} \right] = k \prod_{\text{reactants}} (a_k)^{|\nu_k|} \left[ 1 - \frac{Q}{K} \right] \quad (10)$$

where

$$\prod a_k^{\nu_k} \equiv Q \quad (\Delta_r G \neq 0) ; \quad \prod a_k^{\nu_k} \equiv K \quad (\Delta_r G = 0) \quad (11)$$

The *reaction quotient* has been denoted by  $Q$ . In practical process engineering the authors have found eq. 11 as a useful approximation even for non-elementary reactions, giving an acceptable value for the reaction rate when the activities are known. This will hold true during the path, provided that the necessary LCE assumptions are valid and the rate coefficient  $k$  is known from experiments. The Gibbs energy calculation thus provides the means to deduce the affinities of non-equilibrium reactions and the activities of all constituents in the system through the component potentials.

In practical computation problems, it is of course possible to use other than thermodynamically deduced expressions for the reaction kinetics, including concentration-based, net, or global reaction rate expressions deduced from mechanistic models as well as purely empirical formulations [20,26].

## INTRODUCING REACTION RATE CONSTRAINTS WITH VIRTUAL PHASES

In Table 1, the key properties of the real chemical constituents and virtual phases have been listed. The chemical constituents are those with a true stoichiometric formula, such as, e.g., nitrogen dioxide ( $\text{NO}_2$ ) consisting of one nitrogen and two oxygen atoms, bearing a molecular mass in the respective ratio of its elemental components. The virtual constituent in the conservation matrix appears with zero molecular mass and with zero standard chemical potential, having a stoichiometric factor of +1 for the forward and  $-1$  for the reverse reaction.

**Table 1** Properties related to the virtual components.

| Type of constituent | Stoichiometric elements | Standard state data                    | Molecular mass         |
|---------------------|-------------------------|--|------------------------|
| Chemical            | $c_{kj}$                | $\mu_k^\circ = h_k^\circ - Ts_k^\circ$ | $M_k = \sum c_{kj}M_j$ |
| Virtual (forward)   | +1                      | $\mu_k^\circ = 0$                      | $M_k = 0$              |
| Virtual (reverse)   | -1                      | $\mu_k^\circ = 0$                      | $M_k = 0$              |

The incremental calculation of the progress of a kinetically constrained system is then quite simple. The original input for the system is defined as for any thermodynamic calculation in terms of the initial amounts of substances and the conditions of the  $G = G(T, P, n_k)$  system. The increments due to known reaction rates are deduced from the appropriate reaction rate equations and then introduced to the sequential calculation as initial values of the virtual phases. During the minimization procedure, the molar amounts of reactant and product species of the constrained reactions will adjust according to the incremental changes as obtained from the reaction rate equations and the rest of the system will reach the constrained equilibrium.

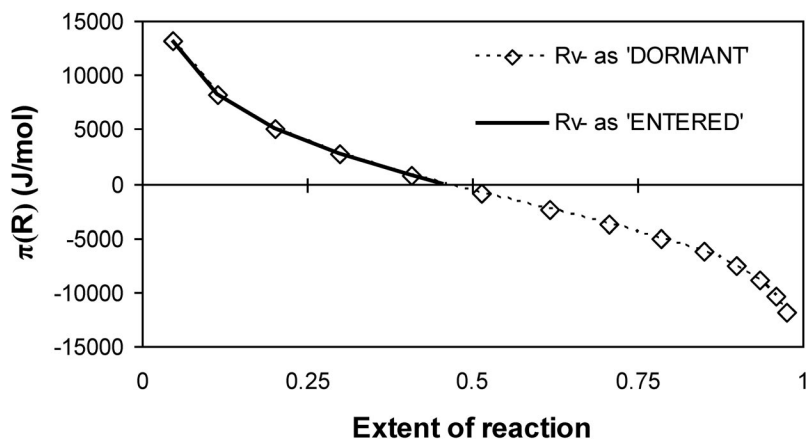
While the Lagrange multiplier (chemical potential) for the constraint component affecting reactant(s) remains positive ( $\pi_{NC'+1} = \pi_R > 0$ ), based on eqs. 8 and 9, it follows that the corresponding affinity  $> 0$  and the net reaction is proceeding. The inequality condition 6 then holds for the Gibbsian calculation. When any of the constraint multipliers becomes zero, the respective constraint entity becomes ineffective. When all of them are zero, affinities of all reactions also are zero and the system has reached chemical equilibrium. Thus, the algorithm provides inherently the thermodynamic equilibrium condition for the kinetically constrained calculation.

It is typical for the Gibbs energy minimizing algorithms that metastability of a phase can be taken into account by suppressing a more stable phase or a given phase constituent from the final calculation, even though it might appear in the given stoichiometric system [25]. In those cases, the algorithms indicate the greater activity of a certain phase, but provide the final calculation for the suppressed metastable system. In ChemApp, the respective identification is “dormant” for the suppressed phase (constituent) and “entered” for the phases allowed to be formed. For the dormant species, however, the activities are calculated using the final (metastable) state as a reference.

Thus, with the “dormancy” of a phase, it is straightforward to follow and control the affinity for the formation of metastability in the system. This feature is extensively used in many conventional minimization algorithms. It is also of practical advantage when performing calculations with the virtual phases in a constrained Gibbs energy system.

For an equilibrium system, eq. 3 can be considered defining a value of the chemical potential also for a species that is not present in the system. It follows that the virtual invariant phases, for which the standard term is zero, can be used for the calculation of alternative reactivity options in systems which

apply reaction rate constraints. The chemical potential of a pure invariant equals zero, when the pure phase appears as “entered” and eq. 5 is valid for a stable phase (the Lagrange multiplier  $\pi_{NC'+1} = \pi_R = 0$ , respectively). When eq. 6 is valid, the phase is not stable and chemical potential of the virtual phase is less than zero. If the calculation is performed in the “dormant” mode, the chemical potential of a virtual feed phase may be less than zero and a forced calculation beyond the equilibrium point becomes possible. This behavior is presented in Fig. 1.



**Fig. 1** Affinity of the kinetically constrained reaction calculated as the Lagrange multiplier of the virtual component. Virtual phase as “entered” reveals the equilibrium point at  $\xi \approx 0.45$  ( $\pi_R = 0$ ). The virtual phase as “dormant” leads to a forced calculation beyond the equilibrium point ( $\pi_R < 0$ ).

## SIMPLE EXAMPLES OF GIBBSIAN SYSTEMS WITH REACTION KINETIC CONSTRAINTS

In the following examples, the basic features of using the reaction rate constraints in Gibbs energy minimization are illustrated. With a simple absorption example, the use of reaction quotient (or affinities) in the computation of aqueous systems is presented by using pH as the thermodynamic control variable. The method then can be generalized for, e.g., industrial solution models.

### Use of the virtual constraints with reaction rates

By adapting the technique of virtual invariant phases, both forward and reverse reactions may be considered and the incremental advancement of chemical reactions can be performed within the Gibbsian calculation. The choice whether the virtual phases appear as “dormant” or “entered” can be used to track the Gibbs energy curve of the reactive system from both sides of the point of equilibrium. This can be illustrated with a simple system often used in modern physical chemistry and thermodynamics textbooks (see, e.g., [29]) as an example for the development of Gibbs energy and affinity in terms the extent of reaction. The decomposition of dinitrogen tetroxide ( $N_2O_4$ ) to nitrogen dioxide ( $NO_2$ ) is a gas-phase reaction occurring with a finite rate in close to ambient temperatures



The rate of  $N_2O_4$  decomposition can be approximated as a first-order reaction as follows

$$\frac{d[N_2O_4]}{dt} = -k[N_2O_4] \Rightarrow \Delta[N_2O_4] = k[N_2O_4] \cdot \Delta t \quad (13)$$

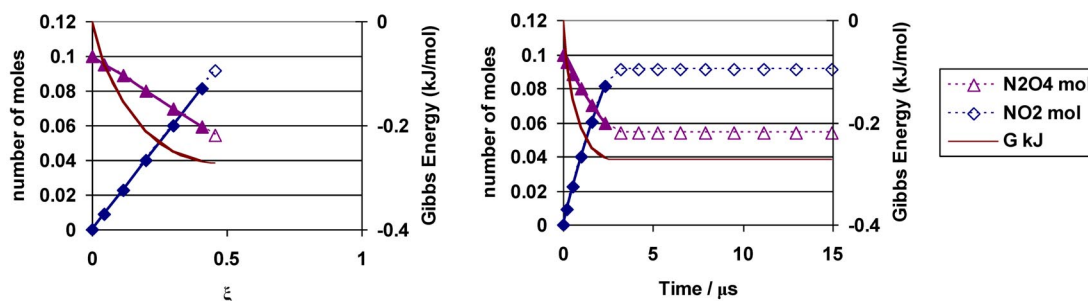
The extended conservation matrix of the simple system is presented in Table 2. The matrix includes nitrogen as an inert gas (not participating in the reaction) and the immaterial component R connected with either forward or reverse reaction via the virtual invariant phases denoted by  $R_{v+}$  and  $R_{v-}$ . The gaseous species have been indicated as (g), the virtual phases appear formally as separate (pure) condensed invariants in the Gibbs energy minimization.

**Table 2** The extended conservation matrix of the  $N_2O_4$  dissociation system.

|             | N | O | R  |
|-------------|---|---|----|
| $N_2(g)$    | 2 | 0 | 0  |
| $N_2O_4(g)$ | 2 | 4 | 1  |
| $NO_2(g)$   | 1 | 2 | 0  |
| $R_{v+}$    | 0 | 0 | 1  |
| $R_{v-}$    | 0 | 0 | -1 |

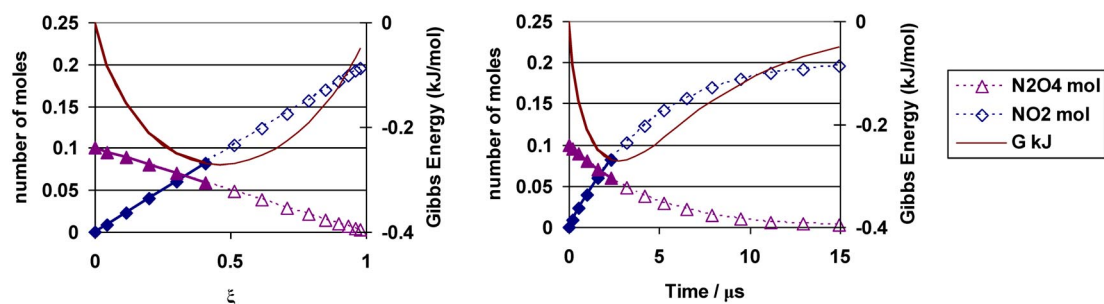
The incremental decomposition of  $N_2O_4$  from eq. 13 is then given as input of  $R_{v-}$  in a sequential calculation. The value of the first-order reaction rate constant  $k$  is from [30];  $A \sim 1.E06 \mu s^{-1}$  and  $E_a \sim 40 \text{ kJ mol}^{-1}$  ( $k = A \cdot \exp[-E_a/(RT)]$ ;  $T$ -range 270–320 K,  $P = 1 \text{ bar}$ ;  $N_2$  is assumed to be the inert gas present).

Based on the conservation matrix, with the input of  $R_{v-}$  in the Gibbsian calculation, the molar amount of  $N_2O_4$  decreases respectively, provided that the virtual phases will not emerge as stable in the minimization calculation. This condition prevails while the inequality (6) is valid ( $\pi_R > 0$ ). This condition is illustrated in Fig. 2 where the virtual invariant phase  $R_{v-}$  has been activated as “entered” in the Gibbs energy calculation. The figures indicate the appearance of the virtual  $R_{v-}$  phase after reaching the  $\min(G)$  value at  $\xi \approx 0.45$ .

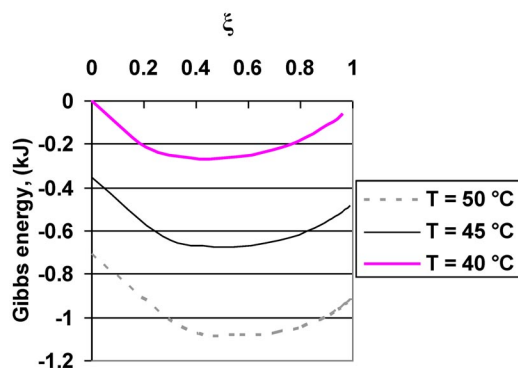


**Figs. 2A,B** Use of the virtual invariant phase with reaction rate constraints in Gibbs energy minimization in the  $N_2/N_2O_4/NO_2$  system. When the virtual phase ( $R_{v-}$  in this case) is used as “entered”, the  $\min(G)$  calculation allows it to form when the equilibrium value of the extent of reaction ( $\xi = \xi_{eq}$ ) has been reached. The energy and mass of the virtual phase are zero by definition, thus its “presence” is virtual without any effect on the physical system. Model input:  $N_2$  2.0 mol (inert);  $N_2O_4$  1.0 mol;  $P = 101 \text{ kPa}$ ,  $T = 40^\circ \text{C}$ .

When the reaction proceeds,  $\pi_R$  equals zero at the equilibrium position and (eq. 5) becomes valid. Thus, the appearance of the virtual invariant phase in the Gibbsian system indicates that equilibrium has been reached. Yet, if the virtual phase is set “dormant” in the system, the full Gibbs energy curve covering the whole range of the extent of reaction ( $0 \leq \xi \leq 1$ ) can be calculated, then forced by eq. 5



**Figs. 3A,B** Use of the virtual phase with reaction rate constraints in Gibbs energy minimization in the  $\text{N}_2/\text{N}_2\text{O}_4/\text{NO}_2$  system. When the virtual phase (Rv–) is used as “dormant”, the  $\min(G)$  calculation proceeds past the equilibrium value of the extent of reaction ( $\xi > \xi_{\text{eq}}$ ), representing composition and Gibbs energy of the system in this range. Model input:  $\text{N}_2$  2.0 mol (inert);  $\text{N}_2\text{O}_4$  1.0 mol;  $P = 101$  kPa,  $T = 40$  °C.



**Fig. 4** Shift of Gibbs energy minimum as function of the temperature calculated by using Rv– as “dormant”.

(Figs. 3 and 4). This feature is practical when, e.g., supersaturated phase conditions or systems with external work need to be simulated.

The reverse reaction (formation of  $\text{N}_2\text{O}_4$ ) could be calculated respectively, by using the virtual phase Rv+ in a similar way. This would of course require the presence of  $\text{NO}_2$  in the initial system, as only reactions consistent with the conservation of all components are allowed.

### Use of the affinity and reaction quotient for reaction rates

In Table 3, a simple aqueous system is described with virtual constraints set for the absorption and desorption of gaseous  $\text{CO}_2$  to and from the aqueous solution.



**Table 3** The extended conservation matrix of the simple CO<sub>2</sub> absorption system.

|                                    | O | H | C | AE | R  |
|------------------------------------|---|---|---|----|----|
| O <sub>2</sub> (g)                 | 2 |   |   |    |    |
| CO <sub>2</sub> (g)                | 2 |   | 1 |    | 1  |
| H <sub>2</sub> O(g)                | 1 | 2 |   |    |    |
| H <sub>2</sub> O                   | 1 | 2 |   |    |    |
| H <sup>+</sup> (aq)                |   | 1 |   | -1 |    |
| OH <sup>-</sup> (aq)               | 1 | 1 |   | 1  |    |
| CO <sub>2</sub> (aq)               | 2 |   | 1 |    |    |
| HCO <sub>3</sub> <sup>-</sup> (aq) | 3 | 1 | 1 | 1  |    |
| CO <sub>3</sub> <sup>2-</sup> (aq) | 3 |   | 1 | 2  |    |
| Rv+                                |   |   |   |    | 1  |
| Rv-                                |   |   |   |    | -1 |

The matrix then allows for the equilibrium between the solute species H<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> as it follows directly from eq. 3 that

$$\mu_{\text{HCO}_3^-} = \mu_{\text{H}^+} + \mu_{\text{CO}_3^{2-}} \quad (14)$$

But, instead of equilibrium of gaseous and aqueous CO<sub>2</sub> we have in terms of the Lagrange multipliers

$$\mu_{\text{CO}_2(\text{aq})} - \mu_{\text{CO}_2(\text{g})} = -\pi_{\text{R}} \quad (15)$$

Equation 15 again defines the affinity of the absorption/desorption of CO<sub>2</sub> in the system. The affinity can be applied with eq. 12 for the reaction rate equation while interpreting, e.g., the pH effect of CO<sub>2</sub> absorption into an aqueous solution. The technique of virtual constraints was then used to model the time development while combining two artificial salt solutions, prepared to observe the effect of mixing to the system pH. The solution A was a saturated solution of CaSO<sub>4</sub> (2.14 g CaSO<sub>4</sub> in 1 kg of water) and the solution B 22.8 mg of CaCO<sub>3</sub> in 1 kg of water. When the clear solutions were mixed the initial pH value was 8.35, which corresponds the given salt solution with 1.62E-6 moles of dissolved CO<sub>2</sub>. The mixing continued in an open vessel at 40 °C for ca. 2 h, during which time a continuous pH drop to 7.66 was observed. This final pH corresponds to the equilibrium pH of such a solution with ambient air. As no precipitation products were observed, it was concluded that the solution absorbed additional CO<sub>2</sub> from the air, which then held the Ca<sup>2+</sup> ions soluble in the system.

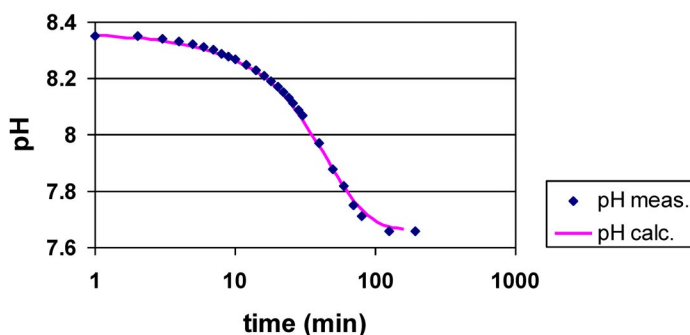
The absorption of CO<sub>2</sub> was described with the simple reaction



for which the reaction rate is  $r = dn_{\text{CO}_2(\text{g})}/dt$ . This can be expressed in terms of the affinity (or reaction quotient) as follows

$$r = k_1 a_{\text{CO}_2(\text{g})} - k_{-1} a_{\text{CO}_2(\text{aq})} = k_1 a_{\text{CO}_2(\text{g})} \left( 1 - \frac{Q}{K} \right) = k_1 a_{\text{CO}_2(\text{g})} \left( 1 - e^{\frac{-A}{RT}} \right) \quad (17)$$

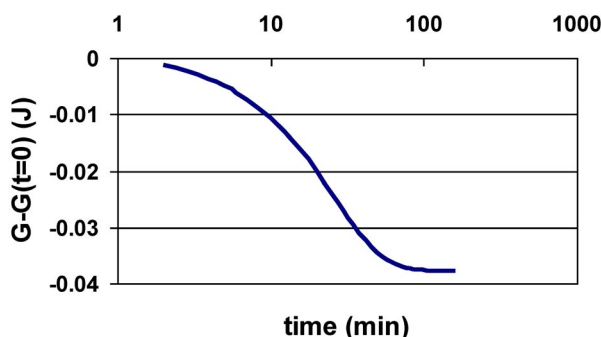
where the affinity  $A$  equals the difference of the molar Gibbs energies of gaseous and dissolved CO<sub>2</sub>. It is assumed that the reactions in the solution are fast when compared to the absorption process, and thus the measured pH value indicates the state of the solution system gradually proceeding toward equilibrium with a large amount of ambient air, consisting of 0.035 % CO<sub>2</sub>. Again, for the practical calculation we adapt the reaction rate as the increase of the virtual component in the system  $r = dn_{\text{CO}_2(\text{g})}/dt \equiv dn_{\text{R}}/dt$ . Adding of the virtual phase Rv- will then reduce the amount of the immaterial component R to the system according to the reaction rate specified by eq. 17. The single reaction rate parameter is the



**Fig. 5** Use of the reaction rate constraint when modelling pH drop due to  $\text{CO}_2$ -absorption into a carbonaceous Ca-sulfate solution. The reaction quotient ( $Q$ ) is used together with the virtual phase input to achieve a smooth approach toward equilibrium. The activities of the aqueous species were calculated in ChemApp by using the Pitzer interaction coefficients [31,32].

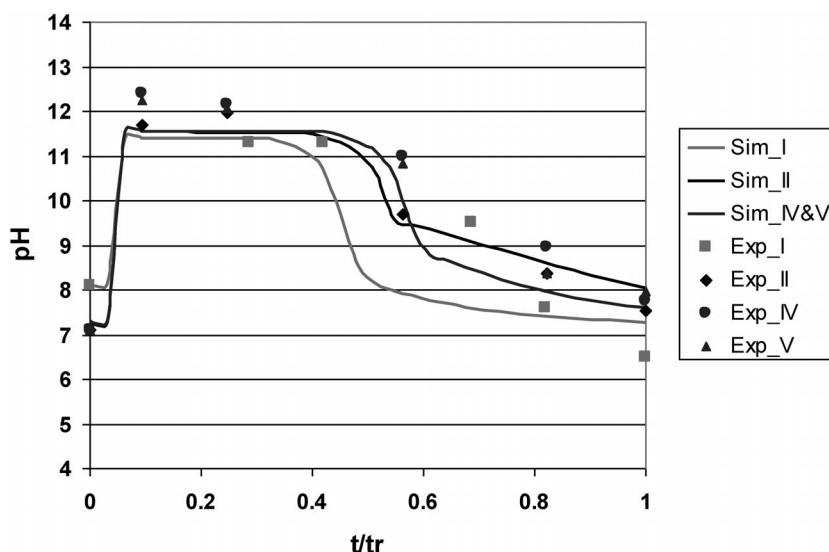
first-order rate coefficient  $k_1$ , which was adjusted to  $1.07\text{E-}3 \text{ mol l}^{-1} \text{ min}^{-1}$  by the measured data. In Fig. 5, the respective calculation result is shown.

In this example, the calculated curve only shows the applicability of the supposed rate equation to the data used for the fitting parameter. From the thermodynamic point of view, the example shows the attainment of the thermodynamic absorption limit in terms of the pH of the solution. The use of the affinity, as received from the Gibbsian method, can be used to recognize the thermodynamic curb in the reaction rate calculation. Figure 6 further shows the monotonically descending  $G = G(t)$  curve for the absorption system.



**Fig. 6** Gibbs energy of the  $\text{CO}_2$  absorption system as function of time.

The method of virtual components in combination with virtual phases gives a practical method to incorporate reaction kinetic constraints to multicomponent-multiphase Gibbs energy calculations. Though the examples here have been confined to problems with only one rate-controlling reaction, the method complies without difficulty for problems with a reduced number of constrained reactions. Figure 7 shows results from a three-phase industrial reaction system for  $\text{CaCO}_3$  production from aqueous  $\text{Ca}(\text{OH})_2$  slurry and  $\text{CO}_2$  gas [26,33]. The rate-determining reactions were deduced to be the dissolution of gaseous  $\text{CO}_2$  and the subsequent  $\text{CaCO}_3$  precipitation. The Gibbsian model with two constrained reactions could thereby give a sufficient description of the reactive behavior. The technique can also be further systematized, and work is in progress to include, e.g., complex biochemical reaction mechanisms to the frame of Gibbs energy computations [20]. In addition, a particular data-assembling



**Fig. 7** The measured (Exp) and modeled (Sim) pH values as a function of the dimensionless reaction time in an industrial  $\text{CaCO}_3$  precipitation reactor [32]. The overall reaction is between a stoichiometric mixture of gaseous  $\text{CO}_2$  and aqueous  $\text{Ca}(\text{OH})_2$  (lime milk). The rate-controlling reactions were chosen as the  $\text{CO}_2$  absorption (as presented in the text) and  $\text{CaCO}_3$  precipitation from  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions. Reaction rate constants were adjusted according to measurement II, the other three were used to validate the Gibbsian model.

program has been developed, so that the input data in connection with the stoichiometric formulations of equilibrium systems can be transmuted to solve problems including kinetic constraints with virtual components and phases [34].

## CONCLUSION

Multiphase Gibbs free energy methods are increasingly used in the simulation of various phenomena, their manifold applications ranging from materials and surface science to chemical engineering, aqueous process solutions, and biochemical processes. The introduction of kinetic constraints allows for the use of rate-determining steps within the thermodynamic system, thus accounting for the simultaneous and interdependent calculation of the chemical and energy changes. In addition to concentrations, the thermodynamic model always provides the activities of constituents, which in several practical problems appear as the important measurable variables. The improved methodology to construct predictive models then also encourages efforts to implement rigorous measurements of thermodynamic and kinetic data from such complex systems.

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