Resolving the speciation model for aqueous carbonate-vanadate system

Complementary to: "Kinetic and mechanistic study of CO_2 absorption into vanadium-promoted aqueous K_2CO_3"

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This text complements the article **Kinetic and mechanistic study of CO_2 absorption into vanadium-promoted aqueous K_2CO_3** [1] by expanding on the speciation model used therein. The accompanying MATLAB script implements the following workflow:

For a given solvent composition (potassium concentration C_K, vanadium concentration C_V, solvent loading θ, and temperature T), the script calculates the corresponding overall mass transfer coefficient K_g, i.e., the CO_2 absorption flux corrected for the driving force and vapor-liquid equilibrium.

To this end, the script first estimates multiple physical parameters, namely, diffusivity D_{CO_2} and Henry constant H of CO_2 in the electrolyte (vanadium-promoted aqueous K_2CO_3), as well as liquid-side mass transfer coefficient k_L, using empirical correlations from the literature. The rate constants k_2 and k_v, describing the reactions of CO_2 with OH^- and HVO_4^{2-} respectively, are then calculated using the kinetic models developed in [1].

Concentrations of OH^- and HVO_4^{2-} are obtained by solving the mass balances and equilibrium relations of the carbonate-vanadate system. These values, together with k_2 and k_v, are used to determine the pseudo-first order rate constant k_1, which in turn yields K_g. For the detailed derivations relating K_g to k_1, solvent composition, and physical properties, the reader is referred to the main article and its supporting material [1].

The remainder of this document describes the procedure for resolving the speciation model of the solvent.

GOVERNING BALANCES AND EQUILIBRIA

An aqueous solution of potassium carbonate and vanadium pentoxide is governed by the following equilibria [2, 3]:

$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$	$K_1 = \frac{[HCO_3^-][H^+]}{[CO_2]}$	$[CO_2] = \frac{[H^+]}{K_1}[HCO_3^-]$	(I)
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$	$[HCO_3^-] = \frac{[H^+]}{K_2}[CO_3^{2-}]$	(II)
$H_2O \rightleftharpoons OH^- + H^+$	$K_w = [OH^-][H^+]$	$[OH^-] = \frac{K_w}{[H^+]}$	(III)
$2H_2VO_4^- \rightleftharpoons V_2O_7^{4-} + 2H^+ + H_2O$	$K_3 = \frac{[V_2O_7^{4-}][H^+]^2}{[H_2VO_4^-]^2}$	$[V_2O_7^{4-}] = \frac{K_3}{[H^+]^2}[H_2VO_4^-]^2$	(IV)
$2H_2VO_4^- \rightleftharpoons HV_2O_7^{3-} + H^+ + H_2O$	$K_4 = \frac{[HV_2O_7^{3-}][H^+]}{[H_2VO_4^-]^2}$	$[HV_2O_7^{3-}] = \frac{K_4}{[H^+]}[H_2VO_4^-]^2$	(V)
$2H_2VO_4^- \rightleftharpoons H_2V_2O_7^{2-} + H_2O$	$K_5 = \frac{[H_2V_2O_7^{2-}]}{[H_2VO_4^-]^2}$	$[H_2V_2O_7^{2-}] = K_5[H_2VO_4^-]^2$	(VI)
$3H_2VO_4^- \rightleftharpoons HV_3O_{10}^{4-} + H^+ + H_2O$	$K_6 = \frac{[HV_3O_{10}^{4-}][H^+]}{[H_2VO_4^-]^3}$	$[HV_3O_{10}^{4-}] = \frac{K_6}{[H^+]}[H_2VO_4^-]^3$	(VII)
$4H_2VO_4^- \rightleftharpoons V_4O_{13}^{6-} + 2H^+ + 3H_2O$	$K_7 = \frac{[V_4O_{13}^{6-}][H^+]^2}{[H_2VO_4^-]^4}$	$[V_4O_{13}^{6-}] = \frac{K_7}{[H^+]^2}[H_2VO_4^-]^4$	(VIII)
$4H_2VO_4^- \rightleftharpoons V_4O_{12}^{4-} + 4H_2O$	$K_8 = \frac{[V_4O_{12}^{4-}]}{[H_2VO_4^-]^4}$	$[V_4O_{12}^{4-}] = K_8[H_2VO_4^-]^4$	(IX)
$5H_2VO_4^- \rightleftharpoons V_5O_{15}^{5-} + 5H_2O$	$K_9 = \frac{[V_5O_{15}^{5-}]}{[H_2VO_4^-]^5}$	$[V_5O_{15}^{5-}] = K_9[H_2VO_4^-]^5$	(X)
$H_3VO_4 \rightleftharpoons H_2VO_4^- + H^+$	$K_{v_1} = \frac{[H_2VO_4^-][H^+]}{[H_3VO_4]}$	$[H_3VO_4] = \frac{[H^+]}{K_{v_1}}[H_2VO_4^-]$	(XI)
$H_2VO_4^- \rightleftharpoons HVO_4^{2-} + H^+$	$K_{v_2} = \frac{[HVO_4^{2-}][H^+]}{[H_2VO_4^-]}$	$[HVO_4^{2-}] = \frac{K_{v_2}}{[H^+]}[H_2VO_4^-]$	(XII)
$HVO_4^{2-} \rightleftharpoons VO_4^{3-} + H^+$	$K_{v_3} = \frac{[VO_4^{3-}][H^+]}{[HVO_4^{2-}]}$	$[VO_4^{3-}] = \frac{K_{v_3}}{[H^+]}[HVO_4^{2-}]$	(XIII)

Complexes between carbonates and vanadates are governed by the following equilibria:

$$\mathrm{H_2VO_4^-} + \mathrm{CO_3^{2-}} + \mathrm{H^+} \rightleftharpoons \mathrm{HVO_4CO_2^{2-}} + \mathrm{H_2O}$$

$$K_{vc_1} = \frac{[\mathrm{HVO_4CO_2^{2-}}]}{[\mathrm{H_2VO_4^-}][\mathrm{CO_3^{2-}}][\mathrm{H^+}]} \qquad [\mathrm{HVO_4CO_2^{2-}}] = K_{vc_1}[\mathrm{H^+}][\mathrm{H_2VO_4^-}][\mathrm{CO_3^{2-}}] \tag{XIV}$$

$$\mathrm{H_2VO_4^-} + 2\mathrm{CO_3^{2-}} + 2\mathrm{H^+} \rightleftharpoons \mathrm{HVO_4(CO_2)_2^{3-}} + 2\mathrm{H_2O}$$

$$K_{vc_2} = \frac{[\mathrm{VO_4(CO_2)_2^{3-}}]}{[\mathrm{H_2VO_4^-}][\mathrm{CO_3^{2-}}]^2[\mathrm{H^+}]^2} \qquad [\mathrm{HVO_4(CO_2)_2^{3-}}] = K_{vc_2}[\mathrm{H^+}]^2[\mathrm{H_2VO_4^-}][\mathrm{CO_3^{2-}}]^2 \tag{XV}$$

Charge, vanadium, and carbon balance respectively give:

$$\begin{aligned} C_\mathrm{K} + [\mathrm{H^+}] = {} & 2[\mathrm{CO_3^{2-}}] + [\mathrm{HCO_3^-}] + [\mathrm{H_2VO_4^-}] + 2[\mathrm{HVO_4^{2-}}] \\ & + 3[\mathrm{VO_4^{3-}}] + 4[\mathrm{V_2O_7^{4-}}] + 3[\mathrm{HV_2O_7^{3-}}] + 2[\mathrm{H_2V_2O_7^{2-}}] \\ & + 4[\mathrm{HV_3O_{10}^{4-}}] + 6[\mathrm{V_4O_{13}^{6-}}] + 4[\mathrm{V_4O_{12}^{4-}}] + 5[\mathrm{V_5O_{15}^{5-}}] \\ & + 2[\mathrm{HVO_4CO_2^{2-}}] + 3[\mathrm{HVO_4(CO_2)_2^{3-}}] + [\mathrm{OH^-}] \end{aligned} \tag{1}$$

$$\begin{aligned} C_\mathrm{V} = {} & [\mathrm{H_3VO_4}] + [\mathrm{H_2VO_4^-}] + [\mathrm{HVO_4^{2-}}] + [\mathrm{VO_4^{3-}}] + 2[\mathrm{V_2O_7^{4-}}] + 2[\mathrm{HV_2O_7^{3-}}] \\ & + 2[\mathrm{H_2V_2O_7^{2-}}] + 3[\mathrm{HV_3O_{10}^{4-}}] + 4[\mathrm{V_4O_{13}^{6-}}] + 4[\mathrm{V_4O_{12}^{4-}}] + 5[\mathrm{V_5O_{15}^{5-}}] \\ & + [\mathrm{HVO_4CO_2^{2-}}] + [\mathrm{HVO_4(CO_2)_2^{3-}}] \end{aligned} \tag{2}$$

$$C_\mathrm{carbon} = \frac{1}{2}C_\mathrm{K}(1+\theta) = [\mathrm{CO_3^{2-}}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_2}] + [\mathrm{HVO_4CO_2^{2-}}] + 2[\mathrm{HVO_4(CO_2)_2^{3-}}] \tag{3}$$

APPROACH FOR SOLVING THE EQUILIBRIA

The system comprises 18 equations (15 mass-action laws, 2 mass balances, and 1 charge balance) for 18 unknown species concentrations (3 carbonates, 11 vanadates, 2 carbonato-vanadate complexes, protons and hydroxides). These are constrained by the given potassium, vanadium, and carbon concentrations, as well as temperature.

A direct solution to this system, while not impossible, is burdensome given the large variation in magnitudes of these species. Instead, we reformulate the problem by selecting a single species concentration, here $\mathrm{H^+}$, as the independent variable. All other concentrations are then back-calculated accordingly. In this way, C_carbon is replaced by pH as the degree of freedom, and the corresponding solvent loading θ is subsequently obtained. Protons concentration (pH) is an ideal degree of freedom due to the large variations in its magnitude with θ.

As demonstrated shortly, for a given pH, the entire equilibria can be reduced into a single equation, which can be solved efficiently using numerical methods. By applying a matrix-based implementation in MATLAB or Python, species concentration and θ are computed across a high-resolution pH grid. The target pH is the obtained by interpolation of this precomputed "database". In the MATLAB script, we provide a working example which follows this algorithm.

SIMPLIFICATION

For a given pH, the concentrations of $\mathrm{H^+}$ and $\mathrm{OH^-}$ are directly obtained as:

$$[\mathrm{H^+}] = 10^{-\mathrm{pH}} \qquad [\mathrm{OH^-}] = K_w/[\mathrm{H^+}] \tag{4}$$

The charge and vanadium balances (eqs. (1) and (2)) are rewritten by substituting the corresponding mass-action laws (eqs. (I)-(XV)), reducing these equations to polynomial functions of $[H_2VO_4^-]$:

$$\begin{aligned}
&C_K + [H^+] - [OH^-] = 2[{CO_3}^{2-}] + \frac{[H^+]}{K_2}[{CO_3}^{2-}] \\
&+ 2K_{vc_1}[H^+][{H_2VO_4}^-][{CO_3}^{2-}] + 3K_{vc_2}[H^+]^2[{H_2VO_4}^-][{CO_3}^{2-}]^2 \\
&+ [{H_2VO_4}^-]\overbrace{\left\{1 + 2\frac{K_{v_2}}{[H^+]} + 3\frac{K_{v_2}K_{v_3}}{[H^+]^2}\right\}}^{\alpha_1} + [{H_2VO_4}^-]^2\overbrace{\left\{4\frac{K_3}{[H^+]^2} + 3\frac{K_4}{[H^+]} + 2K_5\right\}}^{\alpha_2} \\
&+ [{H_2VO_4}^-]^3\underbrace{\left\{4\frac{K_6}{[H^+]}\right\}}_{\alpha_3} + [{H_2VO_4}^-]^4\underbrace{\left\{6\frac{K_7}{[H^+]^2} + 4K_8\right\}}_{\alpha_4} + [{H_2VO_4}^-]^5\underbrace{\{5K_9\}}_{\alpha_5}
\end{aligned} \tag{5}$$

$$\begin{aligned}
&C_V = K_{vc_1}[H^+][{H_2VO_4}^-][{CO_3}^{2-}] + K_{vc_2}[H^+]^2[{H_2VO_4}^-][{CO_3}^{2-}]^2 \\
&+ [{H_2VO_4}^-]\overbrace{\left\{\frac{[H^+]}{K_{v_1}} + 1 + \frac{K_{v_2}}{[H^+]} + \frac{K_{v_2}K_{v_3}}{[H^+]^2}\right\}}^{\beta_1} + [{H_2VO_4}^-]^2\overbrace{\left\{2\frac{K_3}{[H^+]^2} + 2\frac{K_4}{[H^+]} + 2K_5\right\}}^{\beta_2} \\
&+ [{H_2VO_4}^-]^3\underbrace{\left\{3\frac{K_6}{[H^+]}\right\}}_{\beta_3} + [{H_2VO_4}^-]^4\underbrace{\left\{4\frac{K_7}{[H^+]^2} + 4K_8\right\}}_{\beta_4} + [{H_2VO_4}^-]^5\underbrace{\{5K_9\}}_{\beta_5}
\end{aligned} \tag{6}$$

Eqs. (5) and (6) are then subtracted to eliminate the term containing $[CO_3^{2-}]^2$, yielding:

$$\begin{aligned}
&C_K + [H^+] - [OH^-] - 3C_V = [{CO_3}^{2-}]\left\{2 + \frac{[H^+]}{K_2} - K_{vc_1}[H_2VO_4][H^+]\right\} \\
&+ [{H_2VO_4}^-](\alpha_1 - 3\beta_1) + [{H_2VO_4}^-]^2(\alpha_2 - 3\beta_2) + [{H_2VO_4}^-]^3(\alpha_3 - 3\beta_3) \\
&+ [{H_2VO_4}^-]^4(\alpha_4 - 3\beta_4) + [{H_2VO_4}^-]^5(\alpha_5 - 3\beta_5)
\end{aligned} \tag{7}$$

As such, the carbonate concentration can be expressed as a function of $[H_2VO_4^-]$ and $[H^+]$:

$$\begin{aligned}
&[{CO_3}^{2-}] = \{C_K + [H^+] - [OH^-] - 3C_V - [{H_2VO_4}^-](\alpha_1 - 3\beta_1) - [{H_2VO_4}^-]^2(\alpha_2 - 3\beta_2) \\
&- [{H_2VO_4}^-]^3(\alpha_3 - 3\beta_3) - [{H_2VO_4}^-]^4(\alpha_4 - 3\beta_4) - [{H_2VO_4}^-]^5(\alpha_5 - 3\beta_5)\} \\
&\Big/ \left\{2 + \frac{[H^+]}{K_2} - K_{vc_1}[H_2VO_4][H^+]\right\}
\end{aligned} \tag{8}$$

Eq. (8) can be substituted into either the charge balance (eq. (5)) or the vanadium balance (eq. (6)). With $[H^+]$ known, the resulting equations (eqs. (8) and (6) in the MATLAB script) can be solved numerically (e.g., using `fsolve`) for $[H_2VO_4^-]$ given an initial guess $0 < [H_2VO_4^-] < C_V$. Once $[H_2VO_4^-]$ is determined, the remaining species concentrations follow directly from the laws of mass action (eqs. (I)-(XV)). Finally, the carbon balance and solvent loading (eq. (3)) can be calculated.

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