

# Resolving the speciation model for aqueous carbonate-vanadate system

Complementary to: "Kinetic and mechanistic study of CO<sub>2</sub> absorption into vanadium-promoted aqueous K<sub>2</sub>CO<sub>3</sub>"

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This text complements the article **Kinetic and mechanistic study of CO<sub>2</sub> absorption into vanadium-promoted aqueous K<sub>2</sub>CO<sub>3</sub>** [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  $\theta$ , and temperature  $T$ ), the script calculates the corresponding overall mass transfer coefficient  $K_g$ , i.e., the CO<sub>2</sub> absorption flux corrected for the driving force and vapor-liquid equilibrium.

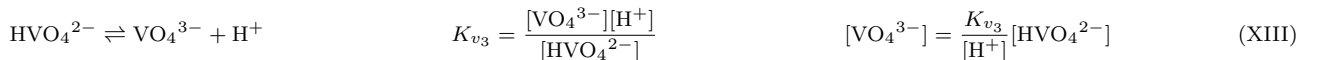
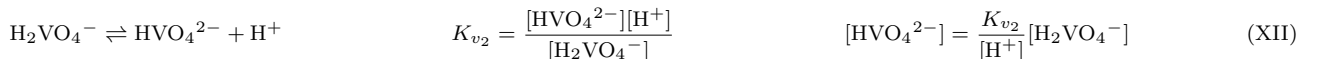
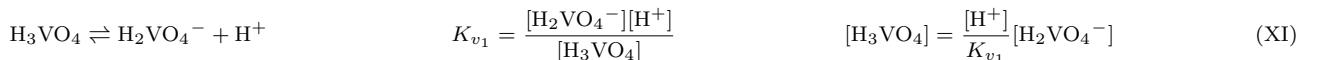
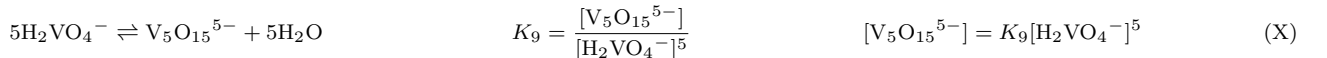
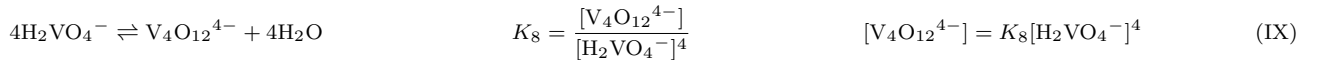
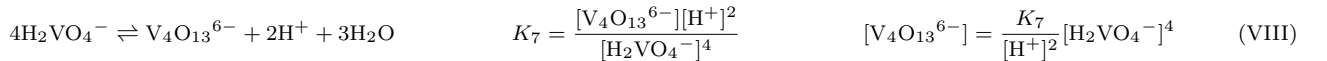
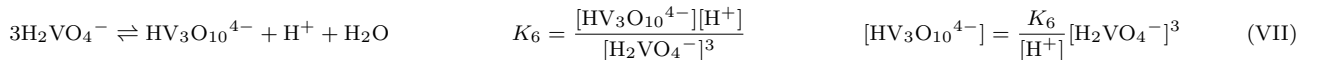
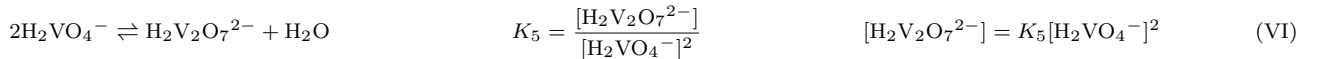
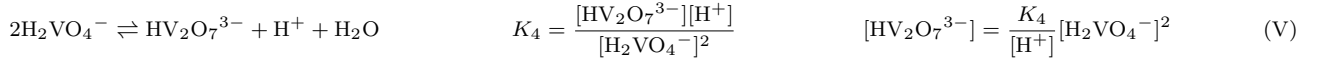
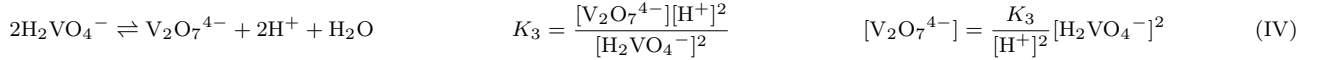
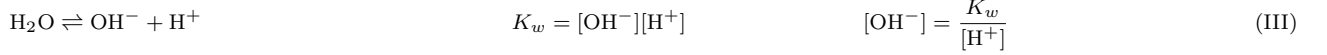
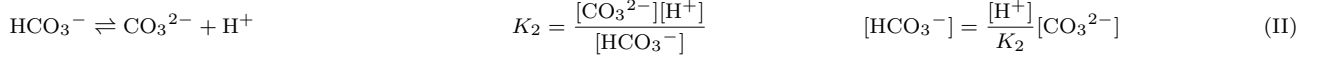
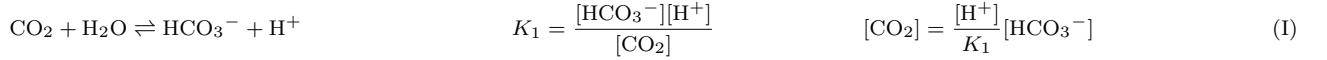
To this end, the script first estimates multiple physical parameters, namely, diffusivity  $D_{\text{CO}_2}$  and Henry constant  $H$  of CO<sub>2</sub> in the electrolyte (vanadium-promoted aqueous K<sub>2</sub>CO<sub>3</sub>), as well as liquid-side mass transfer coefficient  $k_L$ , using empirical correlations from the literature. The rate constants  $k_2$  and  $k_v$ , describing the reactions of CO<sub>2</sub> with OH<sup>-</sup> and HVO<sub>4</sub><sup>2-</sup> respectively, are then calculated using the kinetic models developed in [1].

Concentrations of OH<sup>-</sup> and HVO<sub>4</sub><sup>2-</sup> 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].

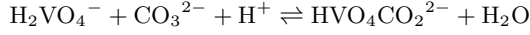
The remainder of this document describes the procedure for resolving the speciation model of the solvent.

## GOVERNING BALANCES AND EQUILIBRIA

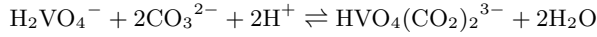
An aqueous solution of potassium carbonate and vanadium pentoxide is governed by the following equilibria [2, 3]:



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



$$K_{vc1} = \frac{[\text{HVO}_4\text{CO}_2^{2-}]}{[\text{H}_2\text{VO}_4^-][\text{CO}_3^{2-}][\text{H}^+]} \quad [\text{HVO}_4\text{CO}_2^{2-}] = K_{vc1}[\text{H}^+][\text{H}_2\text{VO}_4^-][\text{CO}_3^{2-}] \quad (\text{XIV})$$



$$K_{vc2} = \frac{[\text{VO}_4(\text{CO}_2)_2^{3-}]}{[\text{H}_2\text{VO}_4^-][\text{CO}_3^{2-}]^2[\text{H}^+]^2} \quad [\text{HVO}_4(\text{CO}_2)_2^{3-}] = K_{vc2}[\text{H}^+]^2[\text{H}_2\text{VO}_4^-][\text{CO}_3^{2-}]^2 \quad (\text{XV})$$

Charge, vanadium, and carbon balance respectively give:

$$\begin{aligned} C_K + [\text{H}^+] &= 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{VO}_4^-] + 2[\text{HVO}_4^{2-}] \\ &+ 3[\text{VO}_4^{3-}] + 4[\text{V}_2\text{O}_7^{4-}] + 3[\text{HV}_2\text{O}_7^{3-}] + 2[\text{H}_2\text{V}_2\text{O}_7^{2-}] \\ &+ 4[\text{HV}_3\text{O}_{10}^{4-}] + 6[\text{V}_4\text{O}_{13}^{6-}] + 4[\text{V}_4\text{O}_{12}^{4-}] + 5[\text{V}_5\text{O}_{15}^{5-}] \\ &+ 2[\text{HVO}_4\text{CO}_2^{2-}] + 3[\text{HVO}_4(\text{CO}_2)_2^{3-}] + [\text{OH}^-] \end{aligned} \quad (1)$$

$$\begin{aligned} C_V &= [\text{H}_3\text{VO}_4] + [\text{H}_2\text{VO}_4^-] + [\text{HVO}_4^{2-}] + [\text{VO}_4^{3-}] + 2[\text{V}_2\text{O}_7^{4-}] + 2[\text{HV}_2\text{O}_7^{3-}] \\ &+ 2[\text{H}_2\text{V}_2\text{O}_7^{2-}] + 3[\text{HV}_3\text{O}_{10}^{4-}] + 4[\text{V}_4\text{O}_{13}^{6-}] + 4[\text{V}_4\text{O}_{12}^{4-}] + 5[\text{V}_5\text{O}_{15}^{5-}] \\ &+ [\text{HVO}_4\text{CO}_2^{2-}] + [\text{HVO}_4(\text{CO}_2)_2^{3-}] \end{aligned} \quad (2)$$

$$C_{\text{carbon}} = \frac{1}{2}C_K(1 + \theta) = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_2] + [\text{HVO}_4\text{CO}_2^{2-}] + 2[\text{HVO}_4(\text{CO}_2)_2^{3-}] \quad (3)$$

### 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  $\text{H}^+$ , as the independent variable. All other concentrations are then back-calculated accordingly. In this way,  $C_{\text{carbon}}$  is replaced by pH as the degree of freedom, and the corresponding solvent loading  $\theta$  is subsequently obtained. Protons concentration (pH) is an ideal degree of freedom due to the large variations in its magnitude with  $\theta$ .

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  $\theta$  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  $\text{H}^+$  and  $\text{OH}^-$  are directly obtained as:

$$[\text{H}^+] = 10^{-\text{pH}} \quad [\text{OH}^-] = K_w/[\text{H}^+] \quad (4)$$

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  $[\text{H}_2\text{VO}_4^-]$ :

$$\begin{aligned}
C_K + [\text{H}^+] - [\text{OH}^-] &= 2[\text{CO}_3^{2-}] + \frac{[\text{H}^+]}{K_2}[\text{CO}_3^{2-}] \\
&+ 2K_{vc1}[\text{H}^+][\text{H}_2\text{VO}_4^-][\text{CO}_3^{2-}] + 3K_{vc2}[\text{H}^+]^2[\text{H}_2\text{VO}_4^-][\text{CO}_3^{2-}]^2 \\
&+ [\text{H}_2\text{VO}_4^-] \overbrace{\left\{ 1 + 2\frac{K_{v2}}{[\text{H}^+]} + 3\frac{K_{v2}K_{v3}}{[\text{H}^+]^2} \right\}}^{\alpha_1} + [\text{H}_2\text{VO}_4^-]^2 \overbrace{\left\{ 4\frac{K_3}{[\text{H}^+]^2} + 3\frac{K_4}{[\text{H}^+]} + 2K_5 \right\}}^{\alpha_2} \\
&\quad + [\text{H}_2\text{VO}_4^-]^3 \underbrace{\left\{ 4\frac{K_6}{[\text{H}^+]} \right\}}_{\alpha_3} + [\text{H}_2\text{VO}_4^-]^4 \underbrace{\left\{ 6\frac{K_7}{[\text{H}^+]^2} + 4K_8 \right\}}_{\alpha_4} + [\text{H}_2\text{VO}_4^-]^5 \underbrace{\{5K_9\}}_{\alpha_5} \quad (5)
\end{aligned}$$

$$\begin{aligned}
C_V &= K_{vc1}[\text{H}^+][\text{H}_2\text{VO}_4^-][\text{CO}_3^{2-}] + K_{vc2}[\text{H}^+]^2[\text{H}_2\text{VO}_4^-][\text{CO}_3^{2-}]^2 \\
&+ [\text{H}_2\text{VO}_4^-] \overbrace{\left\{ \frac{[\text{H}^+]}{K_{v1}} + 1 + \frac{K_{v2}}{[\text{H}^+]} + \frac{K_{v2}K_{v3}}{[\text{H}^+]^2} \right\}}^{\beta_1} + [\text{H}_2\text{VO}_4^-]^2 \overbrace{\left\{ 2\frac{K_3}{[\text{H}^+]^2} + 2\frac{K_4}{[\text{H}^+]} + 2K_5 \right\}}^{\beta_2} \\
&\quad + [\text{H}_2\text{VO}_4^-]^3 \underbrace{\left\{ 3\frac{K_6}{[\text{H}^+]} \right\}}_{\beta_3} + [\text{H}_2\text{VO}_4^-]^4 \underbrace{\left\{ 4\frac{K_7}{[\text{H}^+]^2} + 4K_8 \right\}}_{\beta_4} + [\text{H}_2\text{VO}_4^-]^5 \underbrace{\{5K_9\}}_{\beta_5} \quad (6)
\end{aligned}$$

Eqs. (5) and (6) are then subtracted to eliminate the term containing  $[\text{CO}_3^{2-}]^2$ , yielding:

$$\begin{aligned}
C_K + [\text{H}^+] - [\text{OH}^-] - 3C_V &= [\text{CO}_3^{2-}] \left\{ 2 + \frac{[\text{H}^+]}{K_2} - K_{vc1}[\text{H}_2\text{VO}_4^-][\text{H}^+] \right\} \\
&+ [\text{H}_2\text{VO}_4^-] (\alpha_1 - 3\beta_1) + [\text{H}_2\text{VO}_4^-]^2 (\alpha_2 - 3\beta_2) + [\text{H}_2\text{VO}_4^-]^3 (\alpha_3 - 3\beta_3) \\
&\quad + [\text{H}_2\text{VO}_4^-]^4 (\alpha_4 - 3\beta_4) + [\text{H}_2\text{VO}_4^-]^5 (\alpha_5 - 3\beta_5) \quad (7)
\end{aligned}$$

As such, the carbonate concentration can be expressed as a function of  $[\text{H}_2\text{VO}_4^-]$  and  $[\text{H}^+]$ :

$$\begin{aligned}
[\text{CO}_3^{2-}] &= \{C_K + [\text{H}^+] - [\text{OH}^-] - 3C_V - [\text{H}_2\text{VO}_4^-] (\alpha_1 - 3\beta_1) - [\text{H}_2\text{VO}_4^-]^2 (\alpha_2 - 3\beta_2) \\
&- [\text{H}_2\text{VO}_4^-]^3 (\alpha_3 - 3\beta_3) - [\text{H}_2\text{VO}_4^-]^4 (\alpha_4 - 3\beta_4) - [\text{H}_2\text{VO}_4^-]^5 (\alpha_5 - 3\beta_5)\} \\
&\quad / \left\{ 2 + \frac{[\text{H}^+]}{K_2} - K_{vc1}[\text{H}_2\text{VO}_4^-][\text{H}^+] \right\} \quad (8)
\end{aligned}$$

Eq. (8) can be substituted into either the charge balance (eq. (5)) or the vanadium balance (eq. (6)). With  $[\text{H}^+]$  known, the resulting equations (eqs. (8) and (6) in the MATLAB script) can be solved numerically (e.g., using `fsolve`) for  $[\text{H}_2\text{VO}_4^-]$  given an initial guess  $0 < [\text{H}_2\text{VO}_4^-] < C_V$ . Once  $[\text{H}_2\text{VO}_4^-]$  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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- [1] N. Mirzaei and M. U. Babler, Kinetic and mechanistic study of  $\text{CO}_2$  absorption into vanadium-promoted aqueous  $\text{K}_2\text{CO}_3$ , Submitted.
- [2] M. Imle, J. Kumelan, D. Speyer, N. McCann, G. Maurer, and H. Hasse, Solubility of carbon dioxide in activated potash solutions in the low and high gas loading regions, *Industrial & Engineering Chemistry Research* **52**, 13477 (2013).
- [3] D. C. Crans and A. S. Tracey, The chemistry of vanadium in aqueous and nonaqueous solution, in *Vanadium Compounds: Chemistry, Biochemistry, and Therapeutic Applications* (ACS Publications, 1998).