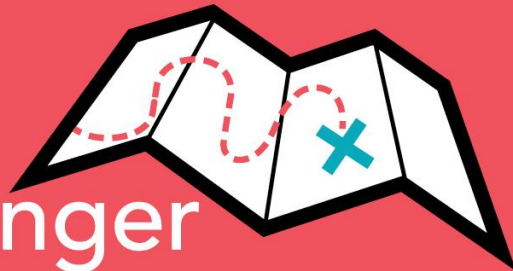


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think simulation

Models for Electrolyte Solutions

Student Workshop at AIChE

November 2019

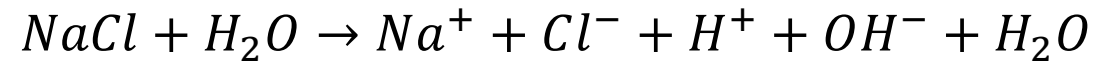
getting the
chemistry right

Calculating pH for Aqueous Solutions

Simple single salt systems may yield many new complexes in aqueous solutions.

Accurate calculation of pH depends on accounting for all the molecules, ions, complexes, and other species that can exist in the system. (i.e. a complete speciation).

Example: Let's study a simple salt solution; **NaCl** in water:



What would be the pH of a 1 m solution of NaCl at 25°C and 1 atm?

Calculating pH for Aqueous Solutions

For this simple NaCl solution, the final concentration of the dissociated species in solution is:

[Na⁺] = 1.0 moles/kg H₂O

[Cl⁻] = 1.0 moles/kg H₂O

[H⁺] = 10⁻⁷ moles/kg H₂O

[OH⁻] = 10⁻⁷ moles/kg H₂O

H₂O = 1.0 kg H₂O

The definition of pH (considering only the concentration value) is:

$$pH = -\log[H^+]$$

Thus, the pH of this solution is:

$$pH = -\log[10^{-7}] = -(-7) = 7$$

pH of a Complex Salt Solution

Now let's look at a more complicated solution.

What is the pH of a 1.0 m $FeCl_3$ solution at 25 °C and 1 atm?

Let's use the simple salt approach first:



The final concentrations would be:

$$[Fe^{3+}] = 1.0 \text{ mole/kgH}_2O$$

$$[Cl^-] = 3.0 \text{ mole/kgH}_2O$$

$$[H^+] = 10^{-7} \text{ moles/kg H}_2O$$

$$[OH^-] = 10^{-7} \text{ moles/kg H}_2O$$

$$H_2O = 1.0 \text{ kg H}_2O$$

And the pH:

$$pH = -\log[10^{-7}] = -(-7) = 7$$

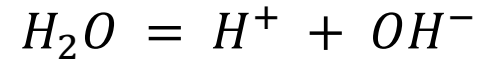
Let's see what the Software tell us...

The Answer: pH = 2.20

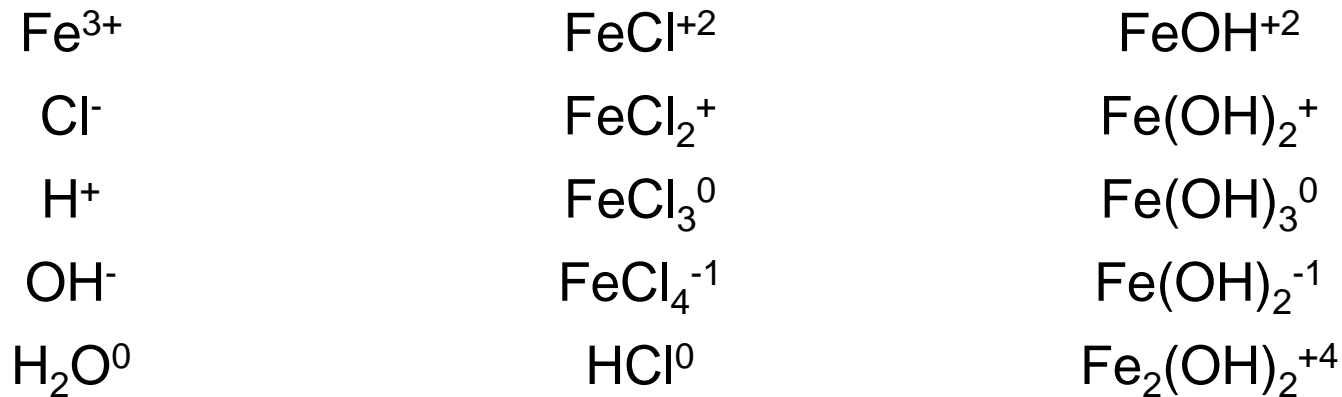
Why is the pH so low?

The aqueous iron species complexes the hydroxide ions. The water dissociation shifts in the direction to replenish the hydroxide ions.

This equilibrium is always present:



Speciation



Speciation of a Complex Salt Solution

Speciation Example:

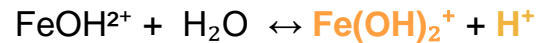
First iron(III) chloride dissociates:



Then the Fe^{3+} interacts with water; hydrolysis reaction:



Then another water molecule enters into the reaction:



Reaction taking up the OH^- from solution, and releasing H^+ into the solution

pH Calculation:

$$pH = -\log(m_{\text{H}^+} \gamma_{\text{H}^+})$$

$$pH = -\log[(5.28940 \times 10^{-3})(1.15211)]$$

$$pH = -\log[6.094 \times 10^{-3}]$$

$$pH = 2.2151$$

Aqueous System Terminology

Electrolyte: A molecular or atomic species (gaseous, liquid, or solid) which has some solubility in water and reacts in water, to some significant extent, to one or more ionic (charged) species. $\text{CO}_2(\text{g})$ and $\text{NaCl}(\text{s})$ are examples of electrolytes.

Nonelectrolyte: A molecular or atomic species (gaseous, liquid, or solid) which has some solubility in water and remains nearly or totally in the molecular form (uncharged) when dissolved in water. $\text{Ar}(\text{g})$ and $\text{C}_6\text{H}_{14}(\text{l})$ are examples of non-electrolytes.

Complex, ion pair: A species composed of both cationic and anionic portions. Complexes can be charged or uncharged. $\text{FeCl}_2^+(\text{aq})$ and $\text{FeCl}_3(\text{aq})$ are examples of complexes.

Strong Electrolyte: A molecular or atomic species which completely dissociates to its constituent base ions, leaving virtually no uncharged molecular forms of the species in water. $\text{KCl}(\text{s})$ and $\text{NaCl}(\text{s})$ at room temperature are examples of electrolytes.

Weak Electrolyte: A molecular or atomic species which partially dissociates in water to its constituent ions, leaving a significant concentration of the molecular forms and/or other complexes. Acetic acid and sulfuric acid are examples of weak electrolytes.

Thermodynamic Properties

Aqueous-phase thermodynamic properties for all species other than water are usually expressed on a partial molal basis. This means that the property is per mole of solution.

The main partial molal thermodynamic properties in electrolyte systems are:

- Gibbs Free Energy, G_i
- Enthalpy, H_i
- Entropy, S_i
- Heat Capacity, Cp_i
- Volume, V_i

Each species in solution possesses a value for each of these properties.

Thermodynamic Properties

Each partial molal thermodynamic property is the sum of the *standard-state* term and the *excess* term.

$$\bar{P}_i = \bar{P}_i^0(T, P) + \bar{P}_i^E(T, P, m) \quad (1)$$

where:

\bar{P}_i represents any partial molal thermodynamic property

\bar{P}_i^0 represents the standard-state term

\bar{P}_i^E represents the excess term

Standard State Term, \bar{P}_i^0

$$\bar{P}_i = \bar{P}_i^0(T, P) + \bar{P}_i^E(T, P, m)$$

This refers to the thermodynamic value of \bar{P}_i^0 at a defined state, i.e. at a defined concentration, temperature and pressure. The non ideal (excess) contribution \bar{P}_i^E are departures from this state.

*For aqueous systems, the standard state refers to a hypothetical 1 m solution of the species extrapolated from **infinite dilution**.*

The standard state is a continuous function of T and P but not a function of composition. This means that for any T and P there is a standard-state value.

Excess Term, \bar{P}_i^E

$$\bar{P}_i = \bar{P}_i^0(T, P) + \bar{P}_i^E(T, P, m)$$

This refers to the thermodynamic value of \bar{P}_i^E and measures the departure of partial molal thermodynamic property from the standard state \bar{P}_i^0 .

The excess term is a function of T, P and composition.

The excess term is related directly to the activity (a_i) and activity coefficient (γ_i) of the species.

Reference State

This refers to the thermodynamic value of \bar{P}_i^R at a specific standard state, i.e. at T=298.15 K and 1 atm.

The reference state is the most common condition for experimental measurements.

Activity (a_i) and Activity Coefficient (γ_i)

Activity, a_i

The activity of a species (a_i), is a thermodynamic property of the species which relates directly to the excess Gibbs free energy:

$$\bar{G}_i^E = RT \ln(a_i) \quad (2)$$

Where:

R is the gas constant

T is the absolute temperature

Activity Coefficient, γ_i

The activity coefficient of a dissolved species (γ_i), is a thermodynamic property of the species which relates directly to the activity:

$$a_i = \gamma_i m_i \quad (3)$$

Where:

m_i is the molality of the species

Symmetric vs Asymmetric Convention

Symmetric

$$\gamma_i \rightarrow 1$$

$$x_i \rightarrow 1$$

Note: This systems would be hardly aqueous. Molality $\rightarrow \infty$

Asymmetric (infinite dilution)

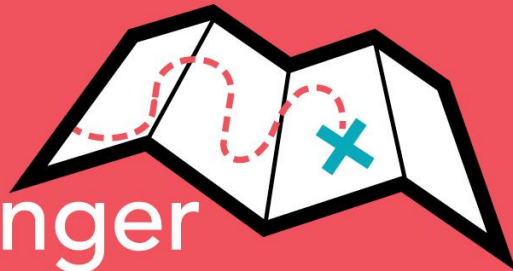
$$\gamma_i \rightarrow 1$$

$$m_i \rightarrow 0$$

Note: Preferred for aqueous systems. Water doesn't have an activity coefficient, γ .

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Five Principal Thermodynamic Properties

Gibbs Free Energy $\bar{G}_i = \bar{G}_i^0 + \bar{G}_i^E$ (4)

Enthalpy $\bar{H}_i = \bar{H}_i^0 + \bar{H}_i^E$ (5)

Heat Capacity $\overline{Cp}_i = \overline{Cp}_i^0 + \overline{Cp}_i^E$ (6)

Entropy $\bar{S}_i = \bar{S}_i^0 + \bar{S}_i^E$ (7)

Volume $\bar{V}_i = \bar{V}_i^0 + \bar{V}_i^E$ (8)

Gibbs Free Energy

The full Gibbs free energy relationship then can be expressed as:

$$\bar{G}_i = \bar{G}_i^0 + RT \ln(\gamma_i m_i) \quad (9)$$

The partial molal Gibbs free energy is also known as the chemical potential.

Note: Another important definition that relates the standard Gibbs free energy with the equilibrium constant of a reaction is:

$$\Delta G^0 = -RT \ln(K)$$

Thermodynamic Equilibrium Relationship

Consider a general stoichiometrically balanced, aqueous-phase equilibrium reaction involving **R** different **aqueous-phase reactant species** and **P** different **aqueous-phase product species**:



For any equilibrium reaction:

$$\sum_{i=1}^r r_i \bar{G}_i = \sum_{i=1}^p p_i \bar{G}_i \quad (11)$$

Where:

r_i is the stoichiometric coefficient of reactant i

p_i is the stoichiometric coefficient of product i

Thermodynamic Equilibrium Relationship

Using the previous equations, (9), (10) and (11), the following expression is obtained:

$$K = \frac{(\gamma_{P_1} m_{P_1})^{p_1} (\gamma_{P_2} m_{P_2})^{p_2} \dots (\gamma_{P_P} m_{P_P})^{p_P}}{(\gamma_{R_1} m_{R_1})^{r_1} (\gamma_{R_2} m_{R_2})^{r_2} \dots (\gamma_{R_R} m_{R_R})^{r_R}} \quad (12)$$

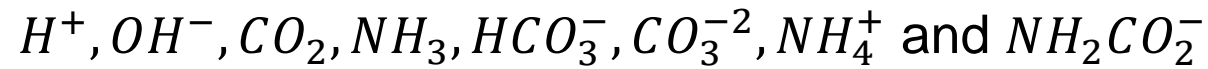
Where K is the equilibrium constant, which is equal to:

$$K = e \left(\frac{- \left[(p_1 \overline{G}_{P_1}^0 + p_2 \overline{G}_{P_2}^0 + \dots + p_P \overline{G}_{P_P}^0) - (r_1 \overline{G}_{R_1}^0 + r_2 \overline{G}_{R_2}^0 + \dots + r_R \overline{G}_{R_R}^0) \right]}{RT} \right) \quad (13)$$

Writing the Mathematical Model

Given: Temperature, pressure, and the relative amounts of the following species: F_{H_2O} , F_{CO_2} and F_{NH_3} .

Calculate: The amount of water (H_2O), and the molalities of the following species:

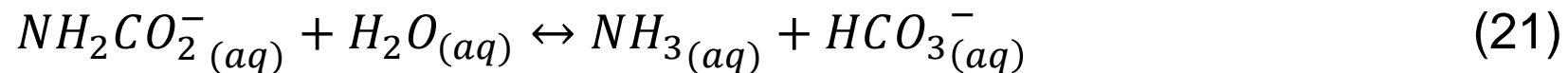
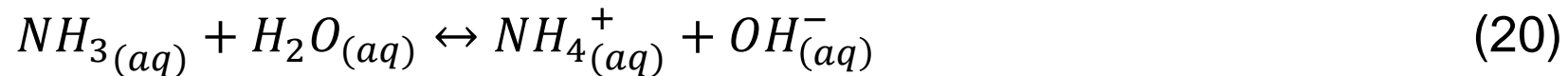
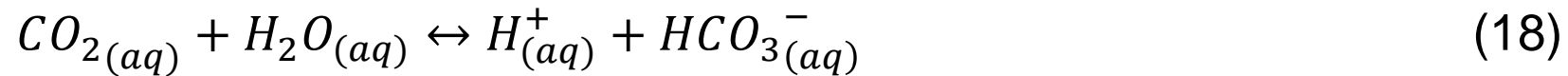


This problem involves the calculation of **9** unknowns.

This means that **9** mathematical equations are needed to solve the problem.

Writing the Mathematical Model

Step 1: Writing a chemical equation of the form of Equation (10) for the independent intraphase equilibrium reactions:



Writing the Mathematical Model

Step 2: Calculate the equilibrium constants (5 equations):

$$K_{H_2O(aq)} = \frac{(\gamma_{H^+} m_{H^+})(\gamma_{OH^-} m_{OH^-})}{a_{H_2O}} \quad (22)$$

$$K_{CO_2(aq)} = \frac{(\gamma_{H^+} m_{H^+})(\gamma_{HCO_3^-} m_{HCO_3^-})}{(\gamma_{CO_2} m_{CO_2}) a_{H_2O}} \quad (23)$$

$$K_{(HCO_3^-)(aq)} = \frac{(\gamma_{H^+} m_{H^+})(\gamma_{CO_3^{2-}} m_{CO_3^{2-}})}{(\gamma_{HCO_3^-} m_{HCO_3^-})} \quad (24)$$

$$K_{NH_3(aq)} = \frac{(\gamma_{NH_4^+} m_{NH_4^+})(\gamma_{OH^-} m_{OH^-})}{(\gamma_{NH_3} m_{NH_3}) a_{H_2O}} \quad (25)$$

$$K_{NH_2CO_2^-(aq)} = \frac{(\gamma_{NH_4^+} m_{NH_4^+})(\gamma_{HCO_3^-} m_{HCO_3^-})}{\gamma_{NH_2CO_2^-} m_{NH_2CO_2^-}} \quad (26)$$

Writing the Mathematical Model

Step 3: Electroneutrality or charge balance equation:

$$m_{H^+} + m_{NH_4^+} = m_{NH_2CO_2^-} + 2 m_{CO_3^{2-}} + m_{HCO_3^-} + m_{OH^-} \quad (27)$$

Note that the sum of the cation concentration on the left-hand side of this equation is equal to the sum of the anion concentrations on the right-hand side.

The concentration of each ion is multiplied by the absolute value of its respective charge.

Writing the Mathematical Model

Step 4: Material balances for H[1+], C[4+], and N[3-]

$$3F_{NH_3} + 2F_{H_2O} = 2H_2O + W_k \left(m_{H^+} + m_{OH^-} + 3m_{NH_3} + 4m_{NH_4^+} + m_{HCO_3^-} + 2m_{NH_2CO_2^-} \right) \quad (28)$$

$$F_{CO_2} = W_k \left(m_{CO_2} + m_{HCO_3^-} + 2m_{NH_2CO_2^-} + m_{CO_3^{2-}} \right) \quad (29)$$

$$F_{NH_3} = W_k \left(m_{NH_3} + m_{NH_4^+} + m_{NH_2CO_2^-} \right) \quad (30)$$

Where $W_k = \left(\frac{\text{moles of water in the system}}{55.508} \right)$ which converts all molalities to moles.

It is assumed that F_{H_2O} , F_{NH_3} and F_{CO_2} are in molal basis.

General Multiphase Mathematical Model

Solid-Electrolyte liquid equilibrium

$$S_i = p_1 P_1 + p_2 P_2 + \dots + p_p P_p \quad (50)$$

The equality of chemical potentials across phases in physical equilibrium is given by:

$$G_{S_i} = \sum_{i=0}^P \overline{G_{P_i}} \quad (51)$$

Expanding, based on earlier relationships, we get the following equation:

$$K_{S_i} = \frac{(\gamma_{P_1} m_{P_1})^{p_1} (\gamma_{P_2} m_{P_2})^{p_2} \dots (\gamma_{P_P} m_{P_P})^{p_P}}{a_S} \quad (52)$$

General Multiphase Mathematical Model

Non Aqueous-Electrolyte liquid equilibrium

$$M_{i,nonaqueous} = M_{i,aqueous} \quad (57)$$

Assumption: Whenever there is equilibrium involving a molecule in a nonaqueous phase (vapor or non-aqueous liquid), there is a corresponding molecule species in the aqueous phase.

The equilibrium is given by:

$$\bar{G}_{naqi} = \bar{G}_{aqi} \quad (58)$$

Using the equilibrium constant form:

$$K_D = \frac{a_{aqi}}{a_{naqi}} \quad (60)$$

General Multiphase Mathematical Model

Vapor Phase-Electrolyte liquid equilibrium

Example to describe the physical vapor-aqueous equilibrium for each molecular species that can form in the vapor phase.

$$M_{i,vapor} = M_{i,aq}$$

The equilibrium is given by (Eq 58):

$$\bar{G}_{i,v} = \bar{G}_{i,aq}$$

Using the equilibrium constant form :

$$K_D = \frac{\gamma_{i,aq} m_{i,aq}}{f_{i,v} y_{i,v} P} \tag{63}$$

Example: Mixing CaCl_2 and HF

- Add a new Stream
 - Rename it **HF**
- Select the AQ Framework
- Add
 - HF – 0.1 moles
- Add a **Single Point** Calculation
- Click **Calculate**. Check pH

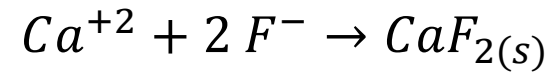
What's the pH of the mixture?

-
- Add a new Stream
 - Rename it **CaCl2**
 - Select the AQ Framework
 - Add
 - CaCl2 – 0.1 moles
 - Add a **Single Point** Calculation
 - Click **Calculate**. Check pH

The pH is 1.44

Why the unusual pH behavior?

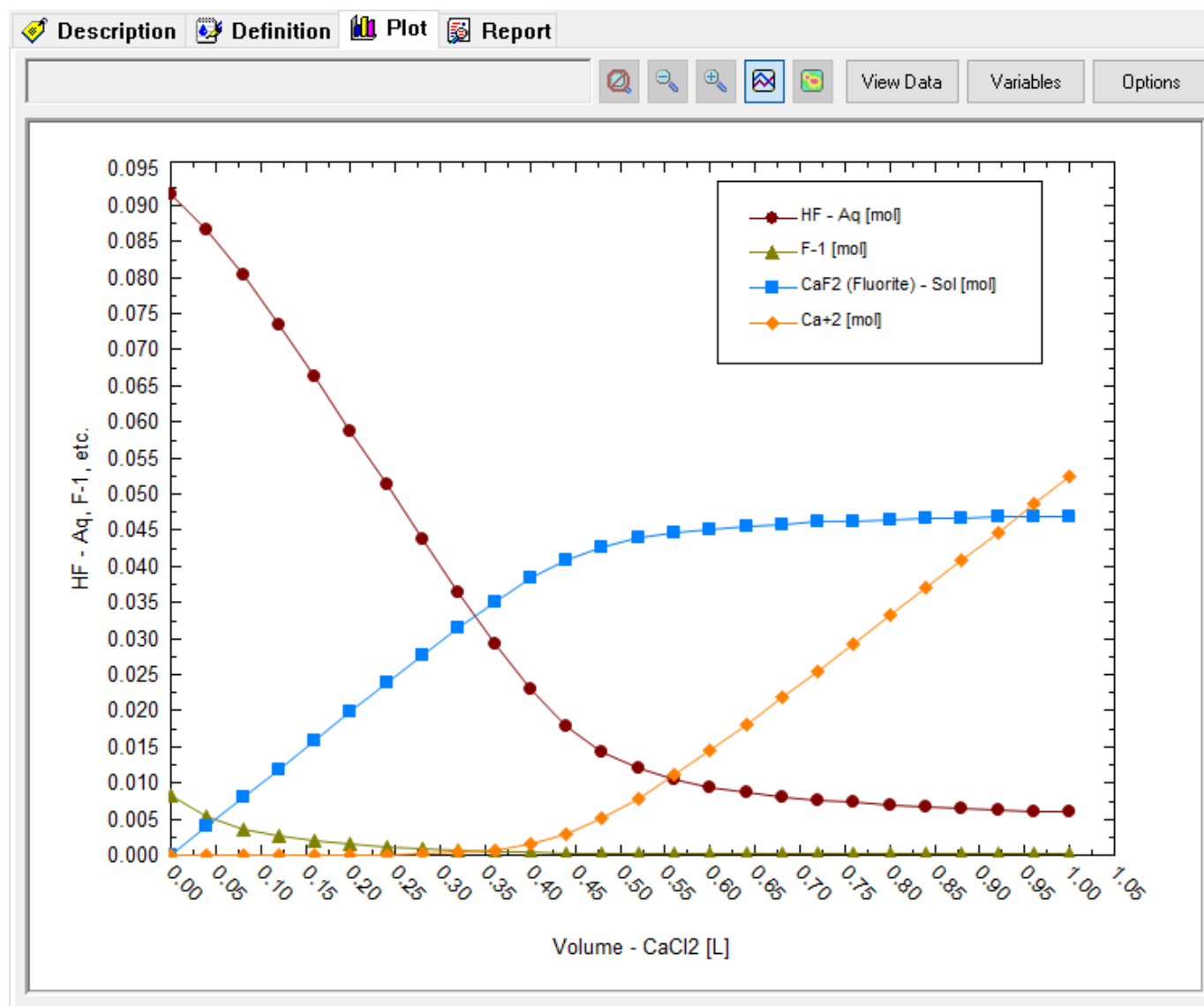
The following reaction occurs:



This shifts the following equilibrium to the right.



CaCl₂ and HF



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