Chemical Equilibrium

A generalized balanced chemical reaction:

\[ aA + bB \rightleftharpoons cC + dD \]

Is this chemical system at equilibrium?

A chemical system is at equilibrium
a. when none of its thermodynamic properties change with time (macroscopic)
b. when the rate of the forward reaction exactly equals the rate of the reverse reaction.

Why is chemical equilibrium important?

All 'chemical transformations' occur because they tend to reach a state of 'chemical equilibrium'.

At equilibrium - microscopically, transformation occur in both directions at equal rates. (dynamic equilibrium).
No changes of macroscopic concentration values occur, if the reaction system is unperturbed from equilibrium 'state'.

At equilibrium all species shown in the equation co-exist, however small/large the concentrations are.

Every system (reaction or otherwise) strives to reach stability, which is the state of equilibrium.

Reactions with very large K are nearly complete (in the forward direction); forward reaction much favored. Amount of product is determined by quantity of limiting reactant only.

Such reactions are ideal for quantitative (gravimetric and volumetric) analysis.

Reactions with very small K have much less tendency to go forward and the reverse reaction is favored!!

A chemical system at equilibrium can be perturbed to a non-equilibrium state. Then the system would readjust to reach a 'new' equilibrium state, in order to offset the disturbance (Le Chaterlier's Principle).

\[ \frac{[C]^e[D]^e}{[A]^l[B]^l} = K \]

\[ [C]^l,[D]^l,... = \text{non-equilibrium concentration values} \]
Any reaction strives to reach the equilibrium state.

\[ aA + bB \rightleftharpoons cC + dD \]

At equilibrium the concentrations of the species would satisfy the equilibrium expression.

\[ K \doteq \frac{[C][D]^c}{[A]^a[B]^b} \]

Reaction species mixed with their concentrations not satisfying the equilibrium concentration expression \((Q \neq K)\) would change their concentrations so as to reach the equilibrium expression values \((Q \rightarrow K)\).

\[ \text{Systems not at equilibrium - Reaction Quotient } Q: \]

\[ Q \doteq \frac{[C][D]^c}{[A]^a[B]^b} \]

\([X] = \text{non-equilibrium (nc) concentration values}\]

\[ aA + bB \rightleftharpoons cC + dD \]

\[ Q = \text{conc. ‘ratio’ of non. eq. system} \leftrightarrow K \]

\[ Q < K \rightarrow Q > K \leftrightarrow \text{non equilibrium: so that } Q = K \text{ i.e. } @equilibrium. \]

For \(K\) and \(Q\) expressions use the numerical value of the concentrations expressed in units of;

- solutions – value of molarity (mol/L) \((\text{std.state} - 1 \text{M})\);
- gases – value of partial pressure (atm) \((\text{std.state} - 1 \text{atm})\);
- for solvents, solids and pure liquids set \([\_] = 1\).

Examples of \(K\) expression:

\[ \text{H}_2\text{CO}_3(\text{aq}) = \text{HCO}_3^{-}(\text{aq}) + \text{H}^{+}(\text{aq}) \]

\[ K = \frac{[\text{HCO}_3^{-}][\text{H}^+]}{[\text{H}_2\text{CO}_3]} \]

\[ \text{Bi}_2\text{S}_3(\text{s}) + 6\text{H}^+(\text{aq}) = 2\text{Bi}^{3+}(\text{aq}) + 3\text{H}_2\text{S}(\text{aq}) \]

\[ K = \frac{[\text{Bi}^{3+}]^2[\text{H}_2\text{S}^3]}{[\text{H}^+]^6} \]

Examples of \(K\) expression:

\[ \text{Manipulating equilibrium constants:} \]

\[ \begin{align*}
aA + bB &= cC + dD \\
K &= \frac{[C][D]^c}{[A]^a[B]^b} \\
cC + dD &= aA + bB; \quad \text{for the reverse reaction} \\
K' &= \frac{[A]^a[B]^b}{[C][D]^c} = \frac{1}{K} \\
K^* &= \frac{1}{K} \end{align*} \]

\[ \begin{align*}
\text{If a reaction is a summation of two or more ‘reactions’; then their equilibrium constants are related;} \\
\begin{cases} 
A + B = C + D \\
C + D + E = F + G \\
A + B + E = F + G
\end{cases} \\
K_1 = \frac{[C][D]}{[A][B]}; \quad K_2 = \frac{[F][G]}{[C][D][E]}; \quad K = \frac{[F][G]}{[A][B][E]} \]

\[ \text{Because (3) = (1) + (2)} \]

\[ K = K_1 K_2 = \frac{[F][G]}{[A][B][E]} \]

\[ K = K_1 K_2 \]
\[ A + B = C + D \quad K_i = \frac{[C][D]}{[A][B]} \]
\[ 2A + 2B = 2C + 2D \quad K = \frac{[C]^2[D]^2}{[A]^2[B]^2} = K_i^2 \]
\[ nA + nB = nC + nD \quad K = \frac{[C][D]}{[A][B]} = K_i^n \]

(Expression for \( K \) is associated with a balanced equation as written).

Aqueous - Solution Chemistry

Most reactions in quantitative analysis are performed in aqueous solutions. Reactants that are generally water soluble are: electrolytes, polar molecules or small molecules.

dissociation: ~100% strong electrolyte
< 1% fairly weak electrolyte

The ions of dissolved weak electrolytes exist in equilibrium with it's un-dissociated molecules.

\[ AB(aq) \rightleftharpoons A^+(aq) + B^-(aq) \]

Examples of equilibria:

**Acid dissociation** \( K_a \):

\[ HA + H_2O \rightleftharpoons A^- + H_3O^+ \] (note: 3 species + solvent) acid

\[ K_{a,HA} = \frac{[A^-][H_3O^+]}{[HA]} \]

conjugate base

note: \([H_2O]\) – solvent; set to 1.

stronger HA (larger \( K_a \)) – weaker base, \( A^- \)
weaker HA (smaller \( K_a \)) – stronger base, \( A^- \)

- \( \log K_a = pK_a \)

**Bronsted Acid** is a substance which increase \([H_3O^+]\) in water.

Strong acids dissociate nearly **completely** in solution.

Strong acids consumes-reacts with basic groups when encountered, almost completely.

Strengths of acids/bases expressed by their \( K \) values.

(only a few strong acids are encountered in aqueous phase)

Know all strong acids and bases. \( K_a > 0 \).

All other acids and bases are weak; \( K_a \) small.

**Table 6.2**: Common Strong Acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>HBr</td>
<td>HBr</td>
<td>Hydrobromic acid</td>
</tr>
<tr>
<td>HI</td>
<td>HI</td>
<td>Hydroiodic acid</td>
</tr>
<tr>
<td>H_2SO_4</td>
<td>H_2SO_4</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>HNO_3</td>
<td>HNO_3</td>
<td>Nitric acid</td>
</tr>
<tr>
<td>HCOOH</td>
<td>HCOOH</td>
<td>Formic acid</td>
</tr>
</tbody>
</table>

**Structure of hydronium ion** \( H_3O^+ \)

Know all strong acids and bases. \( K_a > 0 \).

All other acids and bases are weak; \( K_a \) small.
**Bronsted Base** is a substance which decreases $[\text{H}_3\text{O}^+]$ in water or increases the $[\text{OH}^-]$ in water.

Strong bases consume acidic hydrogens nearly completely, vice versa.

A **salt** is any ionic compound which is **neither a Bronsted acid nor a Bronsted base**.

Strengths of acids/bases expressed by their K values. (only a few strong acids are encountered in aqueous phase)

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**Base constant $K_b$ for a base $A^-$:**

**Bases other than simple hydroxides render aqueous solutions basic due to hydrolysis.** (breakup of water molecules)

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**acid-base reaction $K_{eq}$:**

$$A^- + \text{H}_2\text{O}^+ \rightarrow \text{HA} + \text{H}_2\text{O}$$

$$K_{eq} = \frac{[\text{HA}]}{[A^-] [\text{H}_2\text{O}^+]} = \frac{1}{K_{a_{HA}}}$$

note: inverse relationship

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All **solvents** with active hydrogens (i.e. protic solvents) undergo **auto-protolysis** (self ionization).

$$2\text{NH}_3 = \text{NH}_4^+ + \text{NH}_2^-$$

$$2\text{CH}_3\text{COOH} = \text{CH}_3\text{COOH}_2^- + \text{CH}_3\text{COO}^-$$

$$2\text{H}_2\text{O} = \text{H}_2\text{O}^- + \text{HO}^-$$

Any acid in water (for example) generates hydronium ions. **Acidic species actually available in aqueous solutions is $\text{H}_3\text{O}^+$**.

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*H$_3$O$^+$ ions in solution is hydrated.*

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Hydration shell.

Ideal hydrated hydronium ion.
Auto-protolysis of solvents (water, \(K_w\)):

self dissociation of water: \(2 \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_3\text{O}^+\)

\(K_w = [\text{OH}^-][\text{H}_3\text{O}^+]\)

The strength of an acid or base character of a solute is highly dependent on the solvent in which it is dissolved.

It is the solvent that determines the acid or base strength of a solute.

Leveling effect: All acids stronger than \(\text{H}_3\text{O}^+\) is leveled down to the strength of \(\text{H}_3\text{O}^+\) in water.

All bases stronger than \(\text{HO}^-\) is leveled down to \(\text{HO}^-\) in water.

Weak acids and bases:

acid dissociation \(K_a\) of a weak acid HA:

\[\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+\]

Conjugate pairs shown in color.

Weaker acid → stronger conj. base
Stronger acid → weaker conj. base

\[K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}\]

- \(\log K_a = pK_a\); smaller \(K_a\) ⇔ larger \(pK_a\)

For aqueous solutions:

\[2 \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_3\text{O}^+\] always exist in water

\[K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = [\text{OH}^-][\text{H}^+] = 10^{-14}\] at 25°C

\[K_a \times K_b, \text{A} = K_w\]

Pure water:

\[\text{[H}^+] = [\text{OH}^-] = 10^{-7}\]

\[K_{\text{a,p}} = K_w\]

\[pK_a + pK_b = pK_w\]

\[K_{\text{a,m}} = \frac{K_a}{K_b}\]

stronger conj. Base → weaker acid weaker conj. Base → stronger acid

\[K_{\text{a,s}} = \frac{K_b}{K_a}\]

Weaker acid → stronger conj. base
Stronger acid → weaker conj. base

Solubility of Ionic Compounds

Solubility is an equilibrium process between the ionic compound (solid) and its dissolved ions.

Solubility is expressed as concentrations of solutes in solution at saturation point of dissolution.
Solubility product \(K_{sp}\):

\[ \text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \] \(K_{sp} = 1.1 \times 10^{-10}\)

\(K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]\) "saturated solution" concentrations!!!

no \([\text{BaSO}_4]\) in \(K_{sp}\) expression – solid, set to 1

Compounds with very small \(K_{sp}\) are ideal for gravimetric analysis.

Eqlm. position can be shifted by disturbing the equilibrium system – Le Chaterlier’s Principle.

Note: Reverse of solubilization is precipitation

\[ \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightleftharpoons \text{BaSO}_4(s) \] \(K = \frac{1}{K_{sp}}\)

Note: solubility product gives the concentrations of associated ions existing in equilibrium/their co-existing concentrations.

Reaction quotient, \(Q = \text{conc. product ratio}\) of non-eqlm. system.

For solubility problems note:

\(Q < K \Rightarrow \text{dissolution}\); \(Q = K \Rightarrow \text{eqlm.}\); \(Q > K \Rightarrow \text{pptn.}\)

Example of a solubility equilibrium.

\[ \text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \] \(K = K_{sp}\)

In equilibrium calculations identify the possible equilibria, and pick the concentrations of species relevant to solve the problem.

Calculate \([\text{OH}^-]\) in

\(a. 0.200\text{M NaOH}\)?

\(b. 0.100\text{M HCl}\)?

Solubility of \(\text{Hg}_2\text{Cl}_2\) in

\(a. \text{water}\)?

\(b. 0.030\text{M Cl}^-\)?

\(K_{sp,\text{Hg}_2\text{Cl}_2} = 1.2 \times 10^{-18}\)

\(\text{Hg}_2\text{Cl}_2(s) \rightleftharpoons \text{Hg}_2^{2+}(aq) + 2\text{Cl}^-(aq)\)

Salts are less soluble in solvents carrying common ions - common ion effect!

How much \(\text{Cl}^-\) can be added to a \(\text{Ag}^+\) (0.10 M) solution without creating a precipitate? \(K_{sp,\text{AgCl}} = 1.8 \times 10^{-10}\), i.e. to reach saturation solubility of \(\text{AgCl}\) in water.

\(\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)\)

\[ Q = \frac{[\text{Ag}^+][\text{Cl}^-]}{K_{sp,\text{AgCl}}} \]

What would be the \([\text{Cl}^-]\) so the above system is at equilibrium? That is when would \(Q = K\).

\(Q < K \Rightarrow \text{non-eqlm.: so that } Q < K\) i.e. @eqlm.

\(Q = \frac{[\text{Ag}^+][\text{Cl}^-]}{K_{sp,\text{AgCl}}} = 1.8 \times 10^{-10}\)

\(0.1 \times [\text{Cl}^-] = 1.8 \times 10^{-10}\)

Add \(\text{Cl}^-\) until \([\text{Cl}^-] = 1.8 \times 10^{-9}\)M

\([\text{Cl}^-] = 1.8 \times 10^{-9}\)\(\Rightarrow \text{pptn.}\), \([\text{Cl}^-] > 1.8 \times 10^{-9}\)\(\Rightarrow \text{non-eqlm.}\)

Alternate approach – next page. \(\text{Ag}^+(aq) + \text{Cl}^-(aq) = \text{AgCl}(s)\)
Can you separate Pb(II) 'completely' from Hg(I) from a mixture using iodides? (PbI_2(s), Hg_2I_2(s))?

Initial conc. of both ions Pb(II) and Hg(I) is 0.1M.

K_{sp, lead iodide} = 7.9 \times 10^{-9}
K_{sp, mercury(I) iodide} = 1.1 \times 10^{-28}

Less soluble compound precipitates first.

By inspection, Hg_2I_2 is more insoluble.

In general one must solve for solubility to make that decision.

Criterion: "complete pptn." = 99.99%

At the start of 'complete' precipitation \[ [Hg^+] \] in solution:

\[ [Hg^+] = 0.1 \times \frac{(0.1)^2}{100} = 0.1 \times \frac{0.01}{100} = 10^{-5} \]

The ions in solution (saturation) satisfies;

\[ [Hg^+] [I^-]^2 = K_{sp, Hg_2I_2} \Rightarrow [I^-] = \sqrt{\frac{K_{sp, Hg_2I_2}}{[Hg^+]}} \]

For the system, PbI_2(s) = Pb^2+(aq) + 2I-(aq), at the point of 'complete' precipitation of mercurous ion;

\[ Q_{PbI_2} = [Pb^{2+}][I^-]^2 = [Pb^{2+}]K_{sp, PbI_2} = 0.1 \times 1.1 \times 10^{-28} \]

\[ Q_{PbI_2} = 1.1 \times 10^{-34} < K_{PbI_2} \quad (K_{PbI_2} = 7.9 \times 10^{-9}) \]

no precipitation because no trend to left in the above system.

Would Pb(II) remain in solution when 99.99% of Hg(I) is removed from the solution by precipitation?

If so, at the point of Hg(I) 'removal', the Q for the equilibrium;

\[ PbI_2(s) = Pb^{2+}(aq) + 2I^-(aq) \quad K_{sp, PbI_2} \]

must be less than or equal to it's K value - (K_{sp, PbI_2}) so the equilibrium do not tend to left (i.e. precipitation)

To find out we need to calculate Q_{PbI_2} at the point of 'complete precipitation' of mercurous ion.

Q<K \rightarrow Q>K \leftrightarrow non equilibrium: so that Q=K i.e. @eqlm.

**Complex ions:**
Formation constant of complex ions \( \beta_n \)

In general more than one ligand combines to form metal complexes; occurs when [L]>>0.

\[ M^{x+} + nL \rightarrow ML_n^{x+} \]

overall formation constant \( \beta_n = \frac{[ML_n]}{[M^{x+}][L]^n} \)

All aquated species.

**Stepwise Formation constants, \( K_1, K_2, \ldots, K_n \)**
Complexes are formed in a stepwise manner.

Stepwise equilibria exist.

\[ Pb^{2+} + I^- = PbI^+ \quad K_1 = \frac{[PbI^+]}{[Pb^{2+}][I^-]} \quad [1] \]

\[ PbI^+ + I^- = PbI_2 \quad K_2 = \frac{[PbI_2]}{[PbI^+][I^-]} \quad [2] \]

↑ molecular species

in dissolved state (ion pairs)

\[ PbI_2 + I^- = PbI_3 \quad K_3 = \frac{[PbI_3]}{[PbI_2][I^-]} \quad [3] \]

\[ PbI_3 + I^- = PbI_4^2 \quad K_4 = \frac{[PbI_4^2]}{[PbI_3][I^-]} \quad [4] \]
\( \beta \) - cumulative equilibrium constants

\[
\begin{align*}
[1] & \quad \text{Pb}^{2+} + \Gamma^- = \text{PbI}^- & \beta_1 &= \frac{[\text{PbI}^-]}{[\text{Pb}^{2+}][\Gamma^-]} \\
[1][2] & \quad \text{Pb}^{2+} + 2\Gamma^- = \text{PbI}_2 & \beta_2 &= \frac{[\text{PbI}_2]}{[\text{Pb}^{2+}][\Gamma^-]^2} \\
[1][2][3] & \quad \text{Pb}^{2+} + 3\Gamma^- = \text{PbI}_3 & \beta_3 &= \frac{[\text{PbI}_3]}{[\text{Pb}^{2+}][\Gamma^-]^3} \\
\text{Sum all} & \quad \text{Pb}^{2+} + 4\Gamma^- = \text{PbI}_4^{2-} & \beta_4 &= \frac{[\text{PbI}_4^{2-}]}{[\text{Pb}^{2+}][\Gamma^-]^4}
\end{align*}
\]

Overall formation constant, \( \beta_n = K_1 K_2 \ldots K_n \), is the overall eq. const. of a series of stepwise formation constants \( \beta_i = K_i \).

Equilibrium constants relate the concentrations of species that can coexist at equilibrium (i.e. if the system is not disturbed).

**Polyprotic Acids:**

\[
\begin{align*}
\text{H}_3\text{PO}_4 & \rightleftharpoons \text{H}_2\text{PO}_4^{-1} + \text{H}^+ & K_{1a} \\
\text{H}_2\text{PO}_4^{-1} & \rightleftharpoons \text{HPO}_4^{-2} + \text{H}^+ & K_{2a} \\
\text{HPO}_4^{-2} & \rightleftharpoons \text{PO}_4^{-3} + \text{H}^+ & K_{3a}
\end{align*}
\]

\[
\text{H}_3\text{PO}_4 = \text{HPO}_4^{-2} + 2\text{H}^+ & \quad K_{1b} K_{2a} \\
\text{H}_2\text{PO}_4^{-1} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{PO}_4 + 3\text{H}^+ & K_{3b}
\]

**Polybasic species:**

\[
\begin{align*}
\text{PO}_4^{2-} + \text{H}_2\text{O} & \rightleftharpoons \text{HPO}_4^{-1} + \text{OH}^- & K_{1b} \\
\text{HPO}_4^{-2} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{PO}_4^{-1} + \text{OH}^- & K_{2b} \\
\text{H}_2\text{PO}_4^{-1} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{PO}_4 + \text{OH}^- & K_{3b}
\end{align*}
\]
For triprotic acids:

\[ K_{a1} K_{b3} = K_w \]
\[ K_{a2} K_{b2} = K_w \]
\[ K_{a3} K_{b1} = K_w \]

Note the general fact, that the product of K's of conjugated acid-base pairs in aqueous solution (solvent) is equal to the ion product of water (solvent).

Learn to recognize the acidic and basic entities in large molecules.

**Equivalence point pH - acid/base rxn or pH of salt solutions:**

- **Strong (acids + bases) → salt (e.g. Na\(^+\) + Cl\(^-\)) + water**

- **Weak acid + strong base**
  \[ \text{CH}_3\text{COOH} + \text{Na}^+\text{OH}^- = \text{CH}_3\text{COO}^-\text{Na}^+ + \text{H}_2\text{O} \]
  
  Weak component ↔ (apart from water) a salt of the weak component.

- Overall: the product side is weaker than reactant side, if the reaction takes place as written.

Conjugate base of weaker acid is a stronger base. Conjugate base of stronger acid is a weaker base.

In the above solution:

\[ \text{CH}_3\text{COO}^-\text{, H}_2\text{O, CH}_3\text{COOH, OH}^- \]

Identify all possible equilibria among species

At least one component of such salts reacts with water, hydrolysis;

\[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} = \text{CH}_3\text{COOH} + \text{OH}^- \]

Good base weak acid

At equivalence point; the resultant solution of a weak acid/base titration is not neutral, pH≠7.

i.e. salt of a weak acid or weak base.