

Equilibrium of Brønsted-Lowry reactions

- Acids $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+ \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$
- Bases $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^- \quad K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$
- There is an inverse relationship between the strength of an acid (base) and its conjugate base (acid)
- Chemical reactions *always* proceed from a stronger acid (base) to a weaker acid (base).

Quantification of Acid/Base Strength

- Typically equilibrium constants vary dramatically (from $<10^{-10}$ to $>10^{10}$)
- Chemists thus look at the logarithms

$$pH = -\log[H^+] \quad pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

– Note that pH is not the same as pK_a !

	Acid	Approximate pK_a	Conjugate Base	
Strongest Acid	H ₂ SbF ₆	< -12	SbF ₆ ⁻	Weakest Base
	HI	-10	I ⁻	
	H ₂ SO ₄	-9	HSO ₄ ⁻	
	HBr	-9	Br ⁻	
	HCl	-7	Cl ⁻	
	C ₆ H ₅ SO ₃ H	-6.5	C ₆ H ₅ SO ₃ ⁻	
	(CH ₃) ₂ OH	-3.8	(CH ₃) ₂ O	
	(CH ₃) ₂ C=OH	-2.9	(CH ₃) ₂ C=O	
	CH ₃ OH ₂ ⁺	-2.5	CH ₃ OH	
	H ₃ O ⁺	-1.74	H ₂ O	
	HNO ₃	-1.4	NO ₃ ⁻	
	CF ₃ CO ₂ H	0.18	CF ₃ CO ₂ ⁻	
	HF	3.2	F ⁻	
	H ₂ CO ₃	3.7	HCO ₃ ⁻	
	CH ₃ CO ₂ H	4.75	CH ₃ CO ₂ ⁻	
	CH ₃ COCH ₂ COCH ₃	9.0	CH ₃ COCHCOCH ₃	
	NH ₄ ⁺	9.2	NH ₃	
	C ₆ H ₅ OH	9.9	C ₆ H ₅ O ⁻	
	HCO ₃ ⁻	10.2	CO ₃ ²⁻	
	CH ₃ NH ₃ ⁺	10.6	CH ₃ NH ₂	
	H ₂ O	15.7	OH ⁻	
	CH ₃ CH ₂ OH	16	CH ₃ CH ₂ O ⁻	
	(CH ₃) ₃ COH	18	(CH ₃) ₃ CO ⁻	
	CH ₃ COCH ₃	19.2	⁻ CH ₂ COCH ₃	
	HC≡CH	25	HC≡C ⁻	
	H ₂	35	H ⁻	
	NH ₃	38	NH ₂ ⁻	
	CH ₂ =CH ₂	44	CH ₂ =CH ⁻	
Weakest Acid	CH ₃ CH ₃	50	CH ₃ CH ₂ ⁻	Strongest Base

Equilibrium calculations involving acids and bases

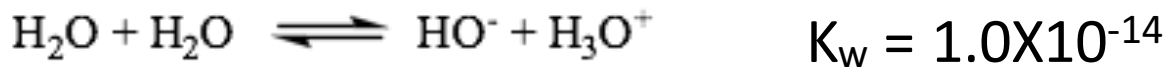
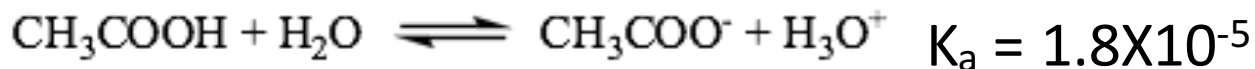
- Typically calculations involve weak acids or bases, as well as dilute solutions
- This means that the degree of dissociation x (how many ions are formed) will be small
- Rule of thumb: x will be small if $[HA]/K_a > 100$ for acids, or if $[B]/K_b > 100$ for bases

Example

- Calculate the pH of a 1.00M solution of acetic acid (CH_3COOH) given a K_a of 1.8×10^{-5} .

Solution

- Although it may not seem obvious at first, there are really two (competing) acid-base reactions here because there are two components in the mixture – acetic acid and water. To decide which one will dominate, we need to look at the K_a 's.



- Because K_a is so much larger than K_w , we can ignore the small amount of H_3O^+ generated by the autoionization of water.

Solution

- Set up the ICE box for the reaction

	CH_3COOH	H_2O	H_3O^+	CH_3COO^-
Initial	1.00		0 (10^{-7})	0
Change	-x		x	x
Equilibrium	1.00-x		x	x

- Set up the expression for K_a and substitute the appropriate values

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

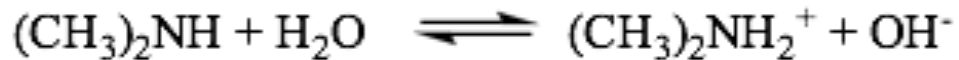
$$1.8 \times 10^{-5} = \frac{x^2}{1.00 - x}$$

Solution

- This is a quadratic equation that must be solved for x . To simplify matters, invoke the “5% rule”
- $[\text{CH}_3\text{COOH}]/K_a = 1.00/1.8 \times 10^{-5} > 100$ so we are justified in considering x to be a small number.
 - Therefore $1-x \approx 1$
- This simplifies the equation to $1.8 \times 10^{-5} = \frac{x^2}{1.00}$ and so $x = 4.2 \times 10^{-3}$ M.
- Since $x = [\text{H}_3\text{O}^+]$, $\text{pH} = -\log[\text{H}_3\text{O}^+] = 2.38$

Example

- The pH of a 0.164M aqueous solution of dimethylamine is 11.98. What are the values of K_b and pK_b ? The ionization equation is



Solution

- In this problem we have to work backwards – we are not given the equilibrium constant but instead are indirectly told the final concentrations of all the species present at equilibrium.
- The expression for K_b will be:

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

- Since we are told the pH we can find $[OH^-]$.
– pH = 11.98 so pOH = 14 - 11.98 = 2.02 and $[OH^-] = 10^{-2.02} = 9.5 \times 10^{-3}$ M.

Solution

- By stoichiometry (or by setting up an ICE box)
 $[(\text{CH}_3)_2\text{NH}_2^+] = [\text{OH}^-] = 9.5 \times 10^{-3} \text{ M}$
- Also, $[(\text{CH}_3)_2\text{NH}]$ at equilibrium will equal the initial concentration minus the amount that dissociates (x):
 $[(\text{CH}_3)_2\text{NH}] = 0.164 - 9.5 \times 10^{-3} \text{ M} = 0.1545$.
- Thus by substituting into the expression for K_b , $K_b = 5.8 \times 10^{-4}$ and $\text{p}K_b = -\log K_b = 3.24$

Theoretical description of the rate laws

- Although the parameters for a rate law are experimentally determined, it is sometimes possible to calculate (or predict) them from first principles. This requires a knowledge of the way in which the reaction takes place, also known as the mechanism.

Theoretical description of the rate laws

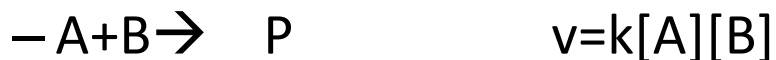
- Most reactions are thought to occur in a series of (relatively) well understood steps, each of which is known as an elementary reaction.
- In an elementary reaction, typically a small number (1-3) atoms, molecules or ions collide with each other and form a product.

Theoretical description of the rate laws

- Molecularity – the number of molecules (or atoms or ions) that come together in an elementary reaction
- Unimolecular- one particle breaks apart or rearranges, i.e. dissociation or isomerization
- Bimolecular- two particles collide with each other
- Termolecular (rare)-three particles simultaneously collide with each other

Theoretical description of the rate laws

- Because elementary reactions are of a known molecularity, we can write down the rate laws for them simply by looking at how many species are present:



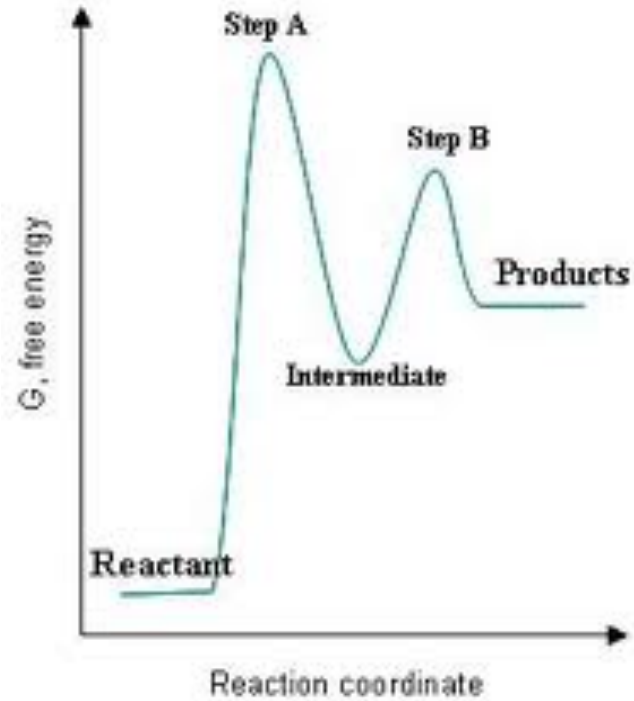
- A mechanism is a combination of elementary reactions that tries to explain the sequence of events (steps) of a chemical reaction

Rate-determining step

- The rate-determining step is the slowest “relevant” step in a chemical reaction, and determines the overall rate of the reaction. It also dictates how much product can be formed.
- Typically the slowest step in a chemical reaction has the highest activation energy since
- In the diagram on the right, the local minima correspond to *intermediates* – this means that they can be (theoretically) isolated.
- The maxima correspond to *transition states* – they are very unstable and not isolable

Rate-determining step

$$k = Ae^{-E_a/RT}$$



Deriving a rate law

- It is often possible to come up with a theoretical rate law, given a mechanism for a reaction (series of elementary reactions), though it might be necessary to invoke steady-state approximations or equilibrium conditions.

Deriving a rate law

- If the mechanism is correct, the rate law should “match” the experimentally determined rate law. However, it is IMPOSSIBLE to prove that the mechanism is correct! All we can say is that the mechanism is consistent with the given data. It is always possible that a different mechanism will also give a result that agrees with the experiment. This is the reason why mechanistic studies are so difficult!

A more complex mechanism

- Now let's consider a reaction where A and B react together, and form an intermediate I, which can then form product P. Furthermore let's assume that the 1st step is in equilibrium:
$$A+B \rightleftharpoons I \longrightarrow P$$

- This is sometimes called a *pre-equilibrium*, because we have to establish equilibrium first between reactants and products before the product can form. It is only possible when the last step (product formation) is the slow step.

A more complex mechanism

- If the forward rate for the 1st step has rate constant k_a , the reverse rate has rate constant k_a' and the 2nd step has rate constant k_b , we can say that pre-equilibrium will exist when $k_a' \gg k_b$.
- We can write down the equilibrium in terms of either the concentrations of A, B and I or in terms of the rate constants:

$$K = \frac{[I]}{[A][B]} = \frac{k_a}{k_a'}$$

A more complex mechanism

- The rate of formation of P will be $\frac{d[P]}{dt} = k_b[I]$
- Using the relationship above we can solve for [I] and express this in terms of more easily measurable quantities (A and B):

$$\frac{d[P]}{dt} = k_b K[A][B] = \frac{k_a k_b}{k_a'} [A][B]$$

- Thus we expect a 2nd order reaction overall, with $k = \frac{k_a k_b}{k_a'}$

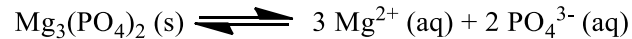
Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.25 M in CH_3NH_2 and 0.10 M in $\text{C}_5\text{H}_5\text{N}$ ($K_b = 1.7 \times 10^{-9}$).

How many grams of $\text{Zn}(\text{CN})_2(\text{s})$ (117.44 g/mol) would be soluble in 100 mL of H_2O ? Include the balanced reaction and the expression for K_{sp} in your answer. The K_{sp} value for $\text{Zn}(\text{CN})_2(\text{s})$ is 3.0×10^{-16} .

Solubility (an equilibrium perspective)

- Solubility product (K_{sp}) – related to the concentrations of the ions involved in a solubility equilibrium (raised to the stoichiometric coefficient)

$$K_{sp} = [\text{Mg}^{2+}]^3[\text{PO}_4^{3-}]^2 = 1.0 \cdot 10^{-25}$$



- K_{sp} is a function of temperature (like all equilibrium constants)

(Incomplete) Table of K_{sp} values

Name	Formula	K_{sp}
Barium carbonate	BaCO ₃	2.6×10^{-9}
Barium chromate	BaCrO ₄	1.2×10^{-10}
Barium sulphate	BaSO ₄	1.1×10^{-10}
Calcium carbonate	CaCO ₃	5.0×10^{-9}
Calcium oxalate	CaC ₂ O ₄	2.3×10^{-9}
Calcium sulphate	CaSO ₄	7.1×10^{-5}
Copper(I) iodide	CuI	1.3×10^{-12}
Copper(II) iodate	Cu(IO ₃) ₂	6.9×10^{-8}
Copper(II) sulphide	CuS	6.0×10^{-37}
Iron(II) hydroxide	Fe(OH) ₂	4.9×10^{-17}
Iron(II) sulphide	FeS	6.0×10^{-19}
Iron(III) hydroxide	Fe(OH) ₃	2.6×10^{-39}
Lead(II) bromide	PbBr ₂	6.6×10^{-6}
Lead(II) chloride	PbCl ₂	1.2×10^{-5}
Lead(II) iodate	Pb(IO ₃) ₂	3.7×10^{-13}
Lead(II) iodide	PbI ₂	8.5×10^{-9}
Lead(II) sulphate	PbSO ₄	1.8×10^{-8}
Magnesium carbonate	MgCO ₃	6.8×10^{-6}
Magnesium hydroxide	Mg(OH) ₂	5.6×10^{-12}
Silver bromate	AgBrO ₃	5.3×10^{-5}
Silver bromide	AgBr	5.4×10^{-13}
Silver carbonate	Ag ₂ CO ₃	8.5×10^{-12}
Silver chloride	AgCl	1.8×10^{-10}
Silver chromate	Ag ₂ CrO ₄	1.1×10^{-12}
Silver iodate	AgIO ₃	3.2×10^{-8}
Silver iodide	AgI	8.5×10^{-17}
Strontium carbonate	SrCO ₃	5.6×10^{-10}
Strontium fluoride	SrF ₂	4.3×10^{-9}
Strontium sulphate	SrSO ₄	3.4×10^{-7}
Zinc sulphide	ZnS	2.0×10^{-25}

- Notice that most values are very small!

Acids and Bases – An Overview

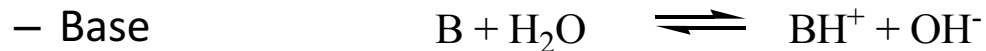
- Arrhenius (1887)
 - Acid = H^+ donor
 - Base = OH^- donor
- Brønsted-Lowry (1923)
 - Acid = H^+ donor
 - Base = H^+ acceptor
- Lewis (1923)
 - Acid = e^- acceptor
 - Base = e^- donor

Arrhenius Theory

- Simplest definition
 - Still commonly used
- Only works for aqueous solutions
- Only works for substances that can generate H^+ (H_3O^+) and OH^- ions
- Based on dissociation
 - Can be used to quantify the *strength* of an acid or base

Brønsted-Lowry

- Equilibrium reactions



- Conjugates
 - Acid and base for reverse reaction
- Conjugate pairs always differ by a single H^+

Brønsted-Lowry

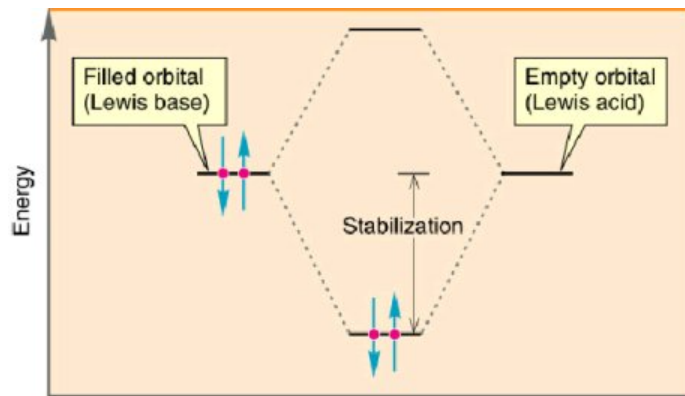
- Amphoterism
 - A substance can sometimes act as either an acid or a base (amphiprotic)



- How do we know which one will happen?
 - Based on *relative strengths* of acids and bases
 - Reactions always go (spontaneously) in the direction of weaker acids/bases

Lewis theory – the MO point of view

- A filled orbital is a Lewis base in that it donates electrons to an unfilled (empty) orbital, which is a Lewis acid



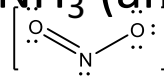
Basic definitions

- Complex – central atom surrounded by ligands
 - Complexes may be neutral or charged (ions)
- Ligands may be neutral or charged
 - Ex. $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoCl}(\text{NH}_3)_5]^{2+}$
- Coordination number – total number of points that ligands connect to central atom
 - Most common numbers are 2, 4 and 6
 - Shapes are given by VSEPR theory (typically linear, tetrahedral, square planar or octahedral)
- Coordination compound – consists of one or more complexes
 - Ex. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$

Ligands

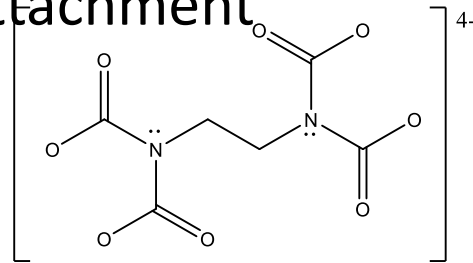
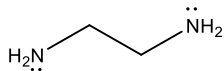
- Generally have lone pairs that can be donated to central atom (Lewis acid)
- The donor atom on the ligand contains the lone pair (Lewis base)

– Ex. Cl^- , OH^- (hydroxo), H_2O (aqua), NH_3 (ammine),
 NO_2^- (nitrito-N or nitrito-O)



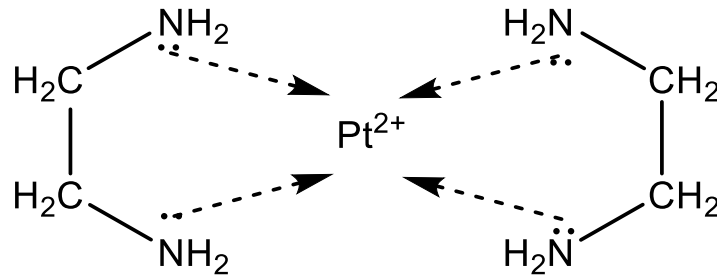
- Ligands can be monodentate, bidentate or polydentate, depending on number of points of attachment

– Ex. Ethylenediamine (en), EDTA



Chelation

- Complex that forms between ligand and metal ion
 - Ex. $[\text{Pt}(\text{en})_2]^{2+}$
 - Square planar geometry



Naming coordination compounds and complex ions

- Name the ligands, followed by the metal
 - Ex. $[\text{Cu}(\text{NH}_3)_4]^{2+}$ = tetraamminecopper(II) ion
- Name the ligands in alphabetical order (ignoring prefixes), listing anionic ligands before neutral ones
 - Ex. $[\text{CoCl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2]^+$ = diamminediaquadichlorocobalt(III) ion
- If the ligand contains a prefix already, use a different prefix for how many ligands there are (bis = 2, tris = 3, tetrakis = 4)
 - Ex. $[\text{Pt}(\text{en})_2]^{2+}$ = bis(ethylenediamine)platinum(II) ion
- Name complex ions by adding –ate at the end (use Latin names for Cu, Au, Fe, Pb, Ag)
 - Ex. $[\text{CuCl}_4]^{2-}$ = tetrachlorocuprate(II) ions
- Common common names – $\text{K}_4[\text{Fe}(\text{CN})_6]$ = potassium ferrocyanide (has Fe^{2+}) and $\text{K}_3[\text{Fe}(\text{CN})_6]$ = potassium ferricyanide (has Fe^{3+})

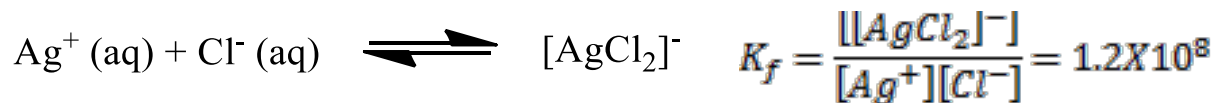
Common-ion Effect?

- Consider the solubility of AgCl in NaCl solutions. You might predict that the aqueous solubility would decrease as the $[\text{Cl}^-]$ increases due to addition of more NaCl. It does, but only up to a point!

$[\text{Cl}^-]$ (M)	Predicted Solubility of AgCl ($\times 10^5$ M)	Measured Solubility of AgCl ($\times 10^5$ M)
0.000	1.3	1.3
0.0039	0.0046	0.072
0.036	0.00050	0.19
0.35	0.000051	1.7
1.4	0.000013	18
2.9	0.0000063	1000

Complex ions

- A complex ion is a polyatomic ion (cation or anion) consisting of a central metal atom (Lewis acid) that has ligands bonded to it (Lewis base) via coordinate covalent bonds.
 - Common ligands include halides, NH_3 and H_2O , with coordination taking place via lone pairs.
- We can describe its formation with a formation constant K_f .
- Ex. $[\text{AgCl}_2]^-$



(Incomplete) Table of K_f values

Table 17.1 Formation Constants for Some Metal Complexions in Water at 25°C		
Complex Ion	K_f	Equilibrium Equation
$\text{Ag}(\text{NH}_3)_2^+$	1.7×10^7	$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$
$\text{Ag}(\text{CN})_2^-$	1×10^{21}	$\text{Ag}^+(aq) + 2\text{CN}^-(aq) \rightleftharpoons \text{Ag}(\text{CN})_2^-(aq)$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	2.9×10^{13}	$\text{Ag}^+(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq)$
CdBr_4^{2-}	5×10^3	$\text{Cd}^{2+}(aq) + 4\text{Br}^-(aq) \rightleftharpoons \text{CdBr}_4^{2-}(aq)$
$\text{Cr}(\text{OH})_4^-$	8×10^{29}	$\text{Cr}^{3+}(aq) + 4\text{OH}^- \rightleftharpoons \text{Cr}(\text{OH})_4^-(aq)$
$\text{Co}(\text{SCN})_4^{2-}$	1×10^3	$\text{Co}^{2+}(aq) + 4\text{SCN}^-(aq) \rightleftharpoons \text{Co}(\text{SCN})_4^{2-}(aq)$
$\text{Cu}(\text{NH}_3)_4^{2+}$	5×10^{12}	$\text{Cu}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(aq)$
$\text{Cu}(\text{CN})_4^{2-}$	1×10^{25}	$\text{Cu}^{2+}(aq) + 4\text{CN}^-(aq) \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}(aq)$
$\text{Ni}(\text{NH}_3)_6^{2+}$	5.5×10^8	$\text{Ni}^{2+}(aq) + 6\text{NH}_3(aq) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(aq)$
$\text{Fe}(\text{CN})_6^{4-}$	1×10^{35}	$\text{Fe}^{2+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}(aq)$
$\text{Fe}(\text{CN})_6^{3-}$	1×10^{42}	$\text{Fe}^{3+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}(aq)$

- Notice that the K_f 's are $\gg 1$

Common Ion Effect

- Specific application of Le Châtelier's Principle to acid-base equilibria.
- If a water-soluble salt is added to a solution that contains a weak acid or base, *and the salt has a common ion with the acid or base*, then the dissociation will be affected by its presence.
- Leads to the idea of a buffer – a solution that contains both forms of a substance (acid and its conjugate base or base and its conjugate acid)

The magical world of buffers

- Buffer (biology definition) – a solution that resists change in pH
- Buffer (chemistry definition) - a solution that is composed of a weak acid and the salt of its conjugate base, or a weak base and the salt of its conjugate acid
- Why are these different ways of saying the same thing?
 - When a small amount of acid(base) is added to a buffer, it will react with the conjugate base(acid) that is present, which will neutralize the solution and only *slightly* change the concentrations of acid and base that are present in the solution

Buffer capacity

- Even though buffers appear to be magical, they cannot resist changes in pH forever!
- In general, the more concentrated a buffer is, the better it will be able to neutralize an incoming acid or base.
- Also in general, the buffer will work best when the concentrations of the conjugate pair (acid and base) are approximately equal.
 - Thus typically buffers are prepared to have a $\text{pH} \approx \text{pK}_a$.