Equilibrium

$A + B \rightarrow C + D$

Dynamic equilibrium occurs in a closed system where there is a balance between the forward and reverse reactions occurring at the same rates. It does not mean that there is an equal amount of reactant and products.

$A + B \rightleftharpoons C + D$

Eg. Two children are perfectly balanced on a teeter-totter. Is this an example of dynamic equilibrium?

No b/c they are not moving.

We will be looking at many different kinds of equilibrium systems such as solubility equilibrium, phase equilibrium, chemical reaction equilibrium and acid-base equilibrium.

The Law of Chemical Equilibrium

The **Law of Chemical Equilibrium** states: At eqm. there is a constant ratio between the concentrations of the products and reactants in any change.

Equilibrium Law Expression: (K_{eq})

For the general chemical reaction: $aA + bB \rightleftharpoons cC + dD$

The equilibrium law expression is: $K_{eq} = \frac{[C]_e^c[D]_e^d}{[A]_e^a[B]_e^b}$ ← products ↙ reactants

where:

[A], [B], [C], and [D] are concentrations in mol/L → @ eqm!

a, b, c, and d are coefficients from the balanced chemical equation

K_{eq} is the equilibrium constant for a given temperature (unitless)

The Meaning of the Magnitude of K

The magnitude of the equilibrium constant provides a measure of the extent to which the reaction has gone to completion when equilibrium is reached.

If K >> 1 $K_e = \frac{[P]}{[R]}$	The reaction proceeds towards completion. The concentrations of products are much greater than the concentrations of reactants at equilibrium.
If K ≅ 1 $K_e = \frac{[P]}{[R]}$	The concentrations of reactants and products are approximately equal at equilibrium.
If K << 1 $K_e = \frac{[P]}{[R]}$	Very small amounts of products formed. The concentrations of reactants are much greater than the concentrations of products at equilibrium.

1. Writing Equilibrium Expressions

NOTE: Concentrations of pure solids and liquids are not written in the equilibrium expression as they cannot change in value

Eg. Write the equilibrium law expression for the reaction in which nitrogen gas reacts with hydrogen gas in a closed system to produce gaseous ammonia as the only product.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$\therefore \quad K_{eq} = \frac{[NH_3]_e^2}{[N_2]_e[H_2]_e^3}$$

pg. 431 #1,3 434 #1, 436 #1

2. Calculating the Equilibrium Constant, K_{eq}

Example: Carbon monoxide reacts with hydrogen to form methanol according to the following equation:

↓ next page

$$CO_{(g)} + 2\,H_{2(g)} \rightleftarrows CH_3OH_{(g)}$$

↙ at

Calculate the value of the equilibrium constant at 327°C if an equilibrium mixture contains the following concentrations of reactants and products: $[CO_{(g)}] = 0.079$ mol/L; $[H_{2(g)}] = 0.158$ mol/L; $[CH_3OH_{(g)}] = 0.021$ mol/L

$K_{eq} = ?$

$$K_{eq} = \frac{[CH_3OH]_e}{[CO]_e[H_2]_e^2}$$

$$= \frac{0.021}{(0.079)(0.158)^2}$$

$$= 11$$

$\therefore K_{eq} = 11$

3. Calculating Equilibrium Concentrations

↙ K_{eq}

Example: At 430°C, the equilibrium constant for the following reaction is 1.84×10^{-2}.

$$2\,HI_{(g)} \rightleftarrows H_{2(g)} + I_{2(g)}$$

If 0.100 mol of hydrogen iodide is placed in a 1.00 L container and allowed to reach equilibrium at this temperature, find the concentrations of each substance at equilibrium. - don't ~~[illegible]~~ Know [eqm] so use ICE table!

②

	$2\,HI_{(g)}$ ⇄	$H_{2(g)}$ +	$I_{2(g)}$
Initial	0.100	0	0
Change	$-2x$	$+1x$	$+1x$
Equilibrium	$0.100-2x$	x	x

① $C = \frac{n}{V} = \frac{0.100}{1.00\,L}$

$= 0.100\,M$

③ $$K_{eq} = \frac{[H_2][I_2]}{[HI]^2}$$

$$1.84\times10^{-2} = \frac{x^2}{(0.100-2x)^2}$$

$$\sqrt{1.84\times10^{-2}} = \sqrt{\frac{x^2}{(0.100-2x)^2}}$$

use "+" so we don't get a "–" concentration →

$$\pm 0.1356 = \frac{x}{(0.100-2x)}$$

$$0.1356(0.100-2x) = x$$

$$0.01356 - 0.2712x = x$$

$$0.01356 = x + 0.2712x$$

$$\frac{0.01356}{1.2712} = \frac{1.2712x}{1.2712x}$$

$x = 1.07\times10^{-2}\ \frac{mol}{L}$

↓ ∴

$[HI]_e = 0.100 - 2x$

$= 0.100 - 2(1.07\times10^{-2}$

$= 7.87\times10^{-2}\ \frac{mol}{L}$

$[H_2]_e = 1.07\times10^{-2}\ \frac{mol}{L}$

$[I_2]_e = 1.07\times10^{-2}\ \frac{mol}{L}$

#4. $N_2O_4 \rightleftharpoons 2NO_2$ $K_{eq} = 4.50$

Find $[N_2O_4]_e$ & $[NO_2]_e$ if $[N_2O_4]_i = 0.50 \frac{mol}{L}$

	N_2O_4	$\rightleftharpoons$	$2NO_2$
I	0.50		0
C	$-x$		$+2x$
E	$0.50-x$		$+2x$

#5 on next page.

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$$

$$4.50 = \frac{(2x)^2}{0.50-x}$$

$$4.50(0.50-x) = 4x^2$$

$$2.25 - 4.50x = 4x^2$$

$$0 = 4x^2 + 4.50x - 2.25 \nearrow \quad x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

$x_1 = 0.375$ ✓ $x_2 = -1.5$ x not valid

$\therefore [N_2O_4]_e = 0.50 - x$

$= 0.50 - 0.375$

$= 0.13$ M

$[NO_2]_e = 2(x) = 2(0.375) = 0.75$ M

pg.427 #1-3,pg.428 #1-5,pg.431 #1-3, pg.434 #1, pg.436 #1-5

Le Chatelier's Principle

When a chemical system at equilibrium is disturbed by a change in a property, the system adjusts in a way that opposes the change.

Concentration

#5.

$$3\,H_2 + N_2 \rightleftharpoons 2\,NH_3 \qquad K_{eq} = 8.00\times10^{-7}$$

Find $[NH_3]_e$ if $[H_2]_e = 0.50\,M$; $[N_2]_e = 1.50\,M$

	$3\,H_2$	$+\;N_2$	$\rightleftharpoons\;2\,NH_3$
I	/	/	0
C			$+2x$
E	0.50	1.50	$+2x$

$$K_{eq} = \frac{[NH_3]_e^2}{[H_2]_e^3\,[N_2]_e}$$

$$8.00\times10^{-7} = \frac{(2x)^2}{(0.50)^3(1.50)}$$

$$8.00\times10^{-7} = \frac{4x^2}{0.1875}$$

$$\frac{1.5\times10^{-7}}{4} = \frac{4x^2}{4}$$

$$\sqrt{3.75\times10^{-8}} = \sqrt{x^2}$$

$$\pm 1.936\times10^{-4}\,M = x$$

$$\therefore\ [NH_3]_e = 2x$$
$$= 2(1.936\times10^{-4})$$
$$= 3.87\times10^{-4}\,M$$
$$= 3.9\times10^{-4}\,M$$

If we increase the concentration, the equilibrium will shift to consume the added reactant/product.

If we decrease the concentration, the equilibrium will shift to produce the removed reactant/product.

Temperature

If we increase the temperature, the equilibrium will shift to consume the added thermal energy.

Exothermic - left Endothermic - right

If we decrease the temperature, the equilibrium will shift to produce the removed thermal energy.

Exothermic - right Endothermic - left

Volume

If we increase the volume (or a decrease in pressure), the equilibrium will shift toward the side with the larger amount of gas molecules. $\uparrow V = \downarrow P$

If we decrease the volume (or an increase in pressure), the equilibrium will shift toward the side with the smaller amount of gas molecules. $\downarrow V = \uparrow P$

Variables That Do Not Affect Equilibrium

If we add a catalyst or an inert gas (noble), there will not be a shift in equilibrium. This is due to the fact that a catalyst is not used up in the reaction and an inert gas will change the pressure, but also will not react with the reactants and products.

Let's look at Pg. 457 #1,2

1. $2\ SO_{3(g)} \rightleftarrows 2\ SO_{2(g)} + O_{2(g)}$ $\Delta H = 197$ kJ → endothermic

What will happen if:

a) $SO_{2(g)}$ is added?

shift left, to consume extra SO_2

b) the pressure is decreased by increasing the volume of the container?

shift right, to produce more gas molecules

c) the pressure is increased by adding $Ne_{(g)}$?

no shift, because Ne is inert.

d) the temperature is decreased?

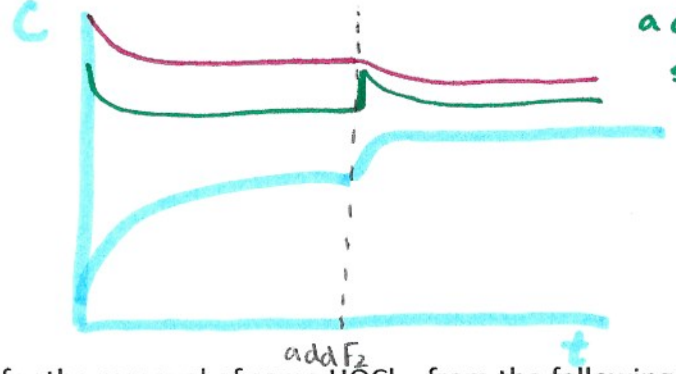
left to produce more heat.

e) $O_{2(g)}$ is removed?

right to produce O_2

2. a) Draw a **concentration-time graph** for the addition of some $F_{2(g)}$ from the following equilibrium:

$Br_{2(g)} + 5\,F_{2(g)} \rightleftarrows 2\,BrF_{5(g)}$

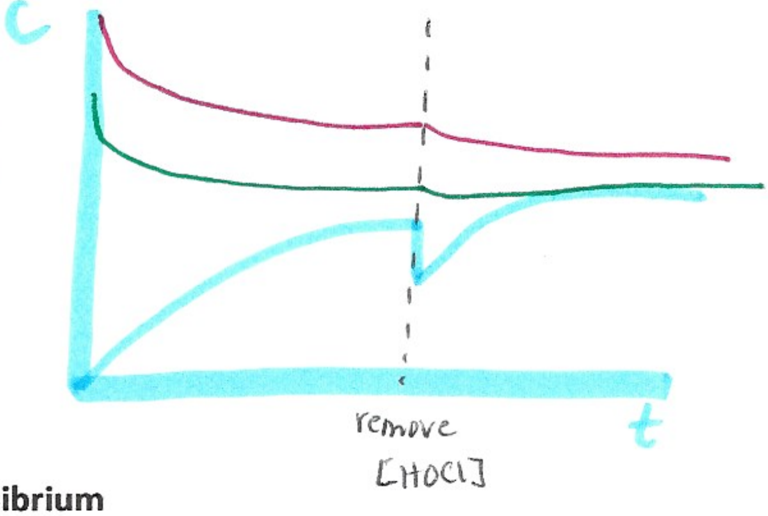


add F_2
shift right
∴ $[Br_2]$↓
$[F_2]$↓
$[BrF_5]$↑

b) Draw a **concentration-time graph** for the removal of some $HOCl_{(g)}$ from the following equilibrium:

$H_2O_{(g)} + Cl_2O_{(g)} \rightleftarrows HOCl_{(g)}$

remove [HOCl]
shift right
$[H_2O]$↓
$[Cl_2O]$↓
[HOCl] ↑



Homework: pg.446 #1-4

Quantitative Changes in Equilibrium

Sometimes we don't know the equilibrium conditions. We must then figure out the reaction quotient, Q, to figure out which way it will shift. It is found the same way as the equilibrium constant, K, only using non-equilibrium values.

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$[C]_i$ $[D]_i$ $[A]_i$ $[B]_i$

initial concentrations

If $Q \overset{\sim}{=} K$, the system is eqm

$Q > K$, the system has more products present and will shift towards the reactants.

$Q < K$, the system has more reactants present and will shift towards the products.

Pg. 464 Example

The following reaction occurs in a closed container at 445°C. The equilibrium constant, K, is 0.020.

$2\,HI_{(g)} \rightleftarrows H_{2(g)} + I_{2(g)}$

Is the system at equilibrium in each of the following cases? If not, predict the direction in which the reaction will proceed to reach equilibrium.

a) $[HI] = 0.14$ mol/L, $[H_2] = 0.04$ mol/L, $[I_2] = 0.01$ mol/L

b) $[HI] = 0.20$ mol/L, $[H_2] = 0.15$ mol/L, $[I_2] = 0.09$ mol/L

a)

$$Q = \frac{[H_2][I_2]}{[HI]^2}$$

$$= \frac{(0.04)(0.01)}{(0.14)^2}$$

$$= 0.0204$$

$Q \overset{\sim}{=} K \therefore$ @ eqm.

b)

$$Q = \frac{[H_2][I_2]}{[HI]^2}$$

$$= \frac{(0.15)(0.09)}{(0.20)^2}$$

$$= 0.3375$$

$Q > K \therefore$ shift left

IN EQUILIBRIUM CALCULATIONS, IF THE RATE CONSTANT, K, IS VERY SMALL AND IF:

[SMALLEST INITIAL]/K > ~~500~~, WE CAN IGNORE THE CHANGE IN x.
100

Pg. 472 Example

Keq ↙ very small!

The decomposition of carbon dioxide has an equilibrium constant of **6.40×10^{-7}** at 2000°C. Calculate the concentrations of all entities at equilibrium if 0.250 mol of $CO_{2(g)}$ is placed in a closed container and heated to 2000°C. assume 1L.

$2\,CO_{2(g)} \rightleftarrows 2\,CO_{(g)} + O_{2(g)}$

① check if @ eqm.

$$Q = \frac{[CO]^2[O_2]}{[CO_2]^2}$$

$$= \frac{(0)^2(0)}{(0.250)^2}$$

$= 0 \quad \therefore Q < K$ shift right

$$2\,CO_2 \rightleftarrows 2\,CO + O_2$$

	$2\,CO_2$	$2\,CO$	O_2
I	0.250	0	0
C	$-2x$	$+2x$	$+x$
E	$0.250-2x$	$2x$	x
**	$\simeq 0.250$		

** $\frac{0.250}{6.40 \times 10^{-7}} >> > 100$

$\therefore$ we can ignore the change in x in $0.250 - 2x$

$$K = \frac{[CO]^2[O_2]}{[CO_2]^2}$$

$$6.40 \times 10^{-7} = \frac{(2x)^2(x)}{(0.250)^2}$$

$$4 \times 10^{-8} = 4x^3$$

$$\sqrt[3]{1 \times 10^{-8}} = \sqrt[3]{x^3}$$

$$x = 2.15 \times 10^{-3}\,M$$

$\therefore [CO_2]_e = 0.250M$

$[CO]_e = 2(2.15 \times 10^{-3})$

$= 4.30 \times 10^{-3}\,M$

$[O_2]_e = 2.15 \times 10^{-3}\,M$

Homework: pg.452 #1-3, pg.454 #1-3, pg.458 #1-3, pg.459 #1-8

Solubility in Equilibrium

When dealing with solubility (amount of solute that can dissolve in a solvent) reactions, the equilibrium constant, K, is called the solubility product constant, K_{sp} (Some common K_{sp} values can be found on pg. 802).

unsaturated – there is less than the maximum amount of solute dissolved in the solvent.

saturated – there is the maximum amount of solute dissolved in the solvent (any more will not dissolve and will stay as solid).

supersaturated – there is more than the maximum amount of solute dissolved in the solvent (there is solid solute not dissolved in the solution.

To find the solubility product constant:

$$\underset{\uparrow}{MgCl_{2(s)}} \rightleftarrows Mg^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

$K_{sp}=[Mg^{2+}][Cl^{-}]^2$ because the $MgCl_2$ is a solid.

Pg. 485

Eg. 1 Magnesium fluoride is a hard, slightly soluble salt that is used to make spectral lenses for technical instruments. Calculate K_{sp} for magnesium fluoride at 25°C, given a solubility of 0.00172 g/100mL.

$MgF_{2(s)} \rightleftarrows Mg^{2+}_{(aq)} + 2F^{-}_{(aq)}$ $\quad K_{sp}=[Mg^{2+}][F^{-}]^2$

① $? \frac{mol}{L} = \frac{0.00172 \cancel{g}}{100 \cancel{mL}} \times \frac{1000 \cancel{ml}}{1L} \times \frac{1 mol}{62.30 \cancel{g}} = 2.76\times10^{-4} \frac{mol}{L} \leftarrow [MgF_2]$

② $\therefore [F^{-}] = 2(2.76\times10^{-4} mol/L) = 5.52\times10^{-4} \frac{mol}{L}$

$\therefore$ ③ $K_{sp} = (2.76\times10^{-4})(5.52\times10^{-4})^2$

$\boxed{K_{sp} = 8.41\times10^{-11}}$

Eg. 2 Calculate the molar solubility of zinc hydroxide at 25°C, where K_{sp} is 7.7×10^{-17}.

$\overset{''}{[\ ]_e}$

① $Zn(OH)_{2(s)} \rightleftarrows Zn^{2+}_{(aq)} + 2OH^{-}_{(aq)}$

E $\quad x \quad 2x$

② $K_{sp} = [Zn^{2+}][OH^{-}]^2$

$7.7\times10^{-17} = x(2x)^2$

$7.7\times10^{-17} = 4x^3$

$x = \sqrt[3]{1.925\times10^{-17}} = 2.7\times10^{-6}$ mol

③ since $Zn^{2+} : Zn(OH)_2 = 1:1$

$\therefore$ molar solubility is 2.7×10^{-6} M

Predicting Precipitation

		Anions						
		Cl^-, Br^-, I^-	S^{2-}	OH^-	SO_4^{2-}	CO_3^{2-}, PO_4^{3-}, SO_3^{2-}	$C_2H_3O_2^-$	NO_3^-
Cations	high solubility (aq) ≥0.1 mol/L (at SATP)	most	Group 1, NH_4^+ Group 2	Group 1, NH_4^+ Sr^{2+}, Ba^{2+}, Tl^+	most	Group 1, NH_4^+	most	all
		All Group 1 compounds, including acids, and all ammonium compounds are assumed to have high solubility in water.						
	low Solubility (s) <0.1 mol/L (at SATP)	Ag^+, Pb^{2+}, Tl^+, Hg_2^{2+} (Hg^+), Cu^+	most	most	Ag^+, Pb^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Ra^{2+}	most	Ag^+	none

pg. 465

Remember that when we have double displacement reactions, we must use the solubility table to predict which product will form a precipitate (if any).

$AB_{(s)} \rightleftharpoons A^+_{(aq)} + B^-_{(aq)}$

With equilibrium reactions, we must calculate the trial ion product, Q, to determine which way the equilibrium will shift.

unsaturated $\text{sol}^{\underline{n}}$.

If $Q < K_{sp}$, the equilibrium will shift right, towards the ions and therefore no precipitate.

$Q = K_{sp}$, we are at equilibrium, therefore there will be no shift and no precipitation & no overall change in [ ] will occur.

$Q > K_{sp}$, the equilibrium will shift left, towards the solid and therefore a precipitate forms & will continue until solution reaches a new equilibrium.

Eg.3 If 100 mL of 0.100 mol/L $CaCl_{2(aq)}$ and 100 mL of 0.0400 mol/L $Na_2SO_{4(aq)}$ are mixed at 20°C, determine whether a precipitate will form. For $CaSO_{4(aq)}$ at 20°C, K_{sp} is 3.6×10^{-5}.

① $CaCl_{2\,(aq)} + Na_2SO_{4\,(aq)} \rightarrow CaSO_{4\,(s)} + 2\,NaCl_{(aq)}$

② $\boxed{CaSO_{4\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}}$, $Q = [Ca^{2+}][SO_4^{2-}]$

③ $CaCl_{2(aq)} \rightarrow Ca^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$

$[Ca^{2+}]$ $C_1V_1 = C_2V_2$

$$C_2 = \frac{C_1V_1}{V_2} = \frac{(0.100M)(0.100L)}{(0.260L)} = 0.05M$$

③ $Na_2SO_{4(aq)} \rightarrow 2Na^+_{(aq)} + SO^{2-}_{4(aq)}$

$$[SO_4^{2-}] = C_2 = \frac{C_1V_1}{V_2} = \frac{(0.04M)(0.1L)}{(0.2L)} = 0.02M$$

④ $Q = (0.05M)(0.02)$

$= 0.001$

$\therefore Q > K$, shift left, ppt. forms!

Common Ion Effect

What if there is a common ion already present in a solution before adding?

Eg. 4 HCl is added to a solution of NaCl. What would happen?

$NaCl_{(s)} \rightleftarrows Na^{+}_{(aq)} + Cl^{-}_{(aq)}$ -common ion

$HCl_{(s)} \rightleftarrows H^{+}_{(aq)} + Cl^{-}_{(aq)}$

If we add HCl, we are adding more Cl⁻ ions into the NaCl equilibrium. Le Chatelier's Principle tells us that this would cause an equilibrium shift __left__ to use up some of the extra Cl⁻. More __ppt__ will be produced.

*+ small

Eg. 5 What is the molar solubility of $PbCl_{2(s)}$ in a 0.2 mol/L $NaCl_{(aq)}$ solution? Ksp $PbCl_2$ is 1.7×10^{-5}.

①

$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$ - common ion

$NaCl_{(s)} \rightleftharpoons Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

0.2 M 0.2 M initial [ ]

∴ ②

	$PbCl_{2(s)}$	$\rightleftharpoons$ $Pb^{2+}_{(aq)}$	+ $2Cl^{-}_{(aq)}$
I	/	0	0.2 M
C	/	+x	+2x
E	/	x	0.2 + 2x ≃ 0.2

$$* \frac{0.2}{1.7 \times 10^{-5}} = 11764 >>> 100$$

$$K_{sp} = [Pb^{2+}][I^{-}]^2$$

$$1.7 \times 10^{-5} = x(0.2)^2$$

$$x = \frac{1.7 \times 10^{-5}}{0.2}$$

$$= 4.25 \times 10^{-4} M$$

$[PbCl_2] : [Pb^{2+}] = 1:1$

$$\boxed{\therefore [PbCl_2] = 4.3 \times 10^{-4} M}$$

Homework pg.462 #1-3, pg.464 #1-4, pg.48 #1-4, pg.470 #1-3, pg.471 #1-11, pg.479 #1-16, pg.480 #1-53,58

Acid-Base Equilibrium

What we know previously:

Acids – H^+ as the cation

- pH from $0 < pH < 7$

Bases - OH^- as the anion

- pH from $7 < pH < 14$

We know that not all acids have H^+ and not all bases have OH^- (eg. NH_3 is a base). Therefore we must use another method to classify an acid and a base.

Recall from gr. 11 ü

↳ **Bronsted-Lowry Acids and Bases** * (always in pairs acid-base)

A Bronsted-Lowry acid is a proton (H) donor. (Has more hydrogens)

A Bronsted-Lowry base is a proton (H) acceptor. (Has less hydrogens)

Eg. 1 $\overset{B.}{NH_3} + \overset{A.}{H_2O} \rightleftarrows \overset{C.A}{NH_4^+} + \overset{C.B}{OH^-}$

reactants have - Base & Acid

Products have - conjugate acid/base

The reactants are called acids and bases while the products are their conjugate acid and base pairs.

A strong acid/base will have a v. weak conjugate base/acid pair, and a very weak acid/base will have a strong conjugate base/acid pair.

~~A weak acid/base will have a ________ conjugate base/acid pair, and a weak acid/base will have a ________ conjugate base/acid pair.~~

If something can both accept and donate protons, it is called amphoteric (or amphiprotic). For example, H_2O.

base→ $H_2O + HCl \rightleftarrows Cl^- + H_3O^+$

acid→ $H_2O + NH_3 \rightleftarrows NH_4^+ + OH^-$

In water, the ion product constant for water, $K_w = 1.0 \times 10^{-14}$ because $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ mol/L.

$$H_2O_{(s)} \rightleftarrows H^+_{(aq)} + OH^-_{(aq)}$$

$$\boxed{K_w = [H^+][OH^-]}$$

$= (1.0 \times 10^{-7}\ \text{mol/L})(1.0 \times 10^{-7}\ \text{mol/L})$

$= 1.0 \times 10^{-14}\ \text{mol/L}$

To find the acidity of a solution, we use the equation for pH:

$\boxed{pH = -\log[H^+]}$

you may have to use more than one of these equations in one question!

We can find the $[H^+]$ by using the equation:

$\boxed{[H^+] = 10^{-pH}}$

If we do not know the $[H^+]$ but we know the $[OH^-]$, we can determine the pOH:

$\boxed{pOH = -\log[OH^-]}$

$0 < pOH < 7$ - base

$7 < pOH < 14$ - acid

We can find the $[OH^-]$ by using the equation:

$\boxed{[OH^-] = 10^{-pOH}}$

Then we can determine the pH by using the equation:

$\boxed{pH + pOH = 14.00}$

Strong Acids and Bases

no equlibrium!!!

Strong acids and bases will completely dissociate to provide H^+ and OH^-.

$HCl_{(l)} \rightleftarrows H^+_{(aq)} + Cl^-_{(aq)}$ $NaOH_{(s)} \rightleftarrows Na^+_{(aq)} + OH^-_{(aq)}$

$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$ $NaOH_{(s)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$

Eg. 2 Determine the pH, pOH, $[OH^-]$ of a 0.042 mol/L solution of HNO_3 (strong acid).

① $HNO_{3(aq)} \longrightarrow H^+ + NO_3^-$

0.042M 0.042M 0.042M

② $pH = -\log[H^+]$

$= -\log(0.042)$

$= 1.38$

④ $[OH^-] = 10^{-pOH}$

$= 10^{-12.62}$

$= 2.5 \times 10^{-13}\ M$

⑤ $pH + pOH = 14$

$pOH = 14 - 1.38$

$= 12.62$

** Weak Acids and Bases ***

Weak acids and bases do not completely dissociate therefore we do not know how much $[H^+]$ or [OH-] dissociates directly. We must use acid and base ionization constants, K_a and K_b, to help us determine this using equilibrium calculations (These values can be found on pg. 803).

Acid: $HA \rightleftarrows H^+_{(aq)} + A^-_{(aq)}$

Base: $BOH \rightleftarrows B^+_{(aq)} + OH^-_{(aq)}$

And $K_a \times K_b = K_w$

Eg. 3 What is the value of the base ionization constant, K_b, for the acetate ion, $C_2H_3O_2^-{}_{(aq)}$? K_a of $HC_2H_3O_2$ (weak acid) is 1.8×10^{-5}.

↙ weak base

acid - K_a
base - K_b

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$= 5.6 \times 10^{-10}$$

Eg. 4 Calculate the hydrogen ion concentration ✓ and the pH ✓ of a 0.10 mol/L acetic acid ($HC_2H_3O_2$) solution. K_a for acetic acid is 1.8×10^{-5} (weak acid).

↓ ✓ Produces H^+

① $HC_2H_3O_{2\,(aq)} \rightleftarrows C_2H_3O_2^- + H^+_{(aq)}$

②

	$HC_2H_3O_2$	$C_2H_3O_2^-$	H^+
I	0.10 M	0	0
C	$-x$	$+x$	$+x$
E	$0.10 - x$ $\simeq 0.10$	x	x

$\frac{0.10}{1.8 \times 10^{-5}} \gg 100$ ✓

③ $$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.10}$$

$$x = \sqrt{(1.8 \times 10^{-5})(0.10)}$$

$$= 1.34 \times 10^{-3}\ M$$

$[H^+] = 1.3 \times 10^{-3}$ M

④ $pH = -\log[H^+]$

$= -\log(1.34 \times 10^{-3})$

$= 2.87$

Eg. 5 Calculate the pH of a 0.100 mol/L aqueous solution of hydrazine ($N_2H_{4(aq)}$, a weak base). The K_b for hydrazine is 1.7 x 10^{-6}.

$$N_2H_4\,(aq) + H_2O_{(l)} \rightleftharpoons N_2H_5^+ + \overset{\text{produces}}{OH^-}$$

↳ turns into OH⁻, so the extra H goes to the other molecule

	$N_2H_4\,(aq)$ ⇌	$N_2H_5^+$ +	OH^-
I	0.100 M	0	0
C	−x	+x	+x
E	0.100 − x ≃ 0.100	x	x

$$\frac{0.100}{1.7\times10^{-6}} \gg 100$$

$$K_b = \frac{[OH^-][N_2H_5^+]}{[N_2H_4]}$$

$$1.7\times10^{-6} = \frac{x^2}{0.100}$$

$$x = \sqrt[2]{(1.7\times10^{-6})(0.100)}$$

$$x = 4.1\underline{2}\times10^{-4}\ M$$

$$[OH^-] = 4.1\underline{2}\times10^{-4}\ M$$

$$\therefore\ pOH = -\log(4.1\underline{2}\times10^{-4})$$

$$= 3.38\underline{5}$$

$$pH = 14.00 - 3.38\underline{5}$$

$$pH = 10.62$$

Homework: pg.492 #1-2, pg.493 #1, pg.494 #1-10, pg.502 #1-2,pg.505 #1-3, pg.508 #1-4, pg.509 #1-10, pg.513 #1-2, pg.520 #1-2, pg.521 #1-2, pg.524 #1-2, pg.525 #1-10, pg.527 #1-2, pg.529 #1-3, pg.530 #1-10, pg.536 #1-2, pg.538 #1-2, pg.539 #1-6

Titration

A titration is a precise addition of a solution to another solution. We use this technique when neutralizing an acid with a base or vice versa. In a titration, there are two main points that must be observed and measured:

Equivalence point – the amount of reactant added is the same as the amount consumed by the sample. Or the number of moles of acid equals the number of moles of base.

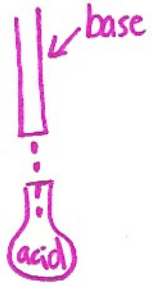
Endpoint – the point where a sharp change occurs. In neutralizations, this is usually a colour change by the indicator. This change occurs so quickly that the endpoint is usually an approximation as indicators have a pH range when they show a change, not a precise value.

We will be looking at two different titration situations: Strong-Strong ~~and Strong-Weak.~~

Titration of a Strong Acid with a Strong Base

In a strong acid and strong base titration, we know that both the acid and base will completely dissociate. This makes the equilibrium calculations straightforward.

Let's look at a titration of 20.00 mL of a 0.300 mol/L $HCl_{(aq)}$ solution with a 0.300 mol/L $NaOH_{(aq)}$ solution. We will calculate the pH of the system at 4 different stages. ***



a) Before Titration – 0 mL of NaOH

Before titration, there is only HCl present in the solution. Therefore to find the pH of the solution: strong acid!

$$HCl_{(aq)} \text{--->} H^+_{(aq)} + Cl^-_{(aq)}$$

$$[H^+] = [HCl]$$
$$= 0.300\,M \text{ because } 1:1$$

$$pH = -\log[H^+]$$
$$= -\log(0.300)$$
$$= 0.500$$

This makes sense as there is only a strong acid solution present.

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

b) Before Equivalence Point – 10.00 mL NaOH

Before equivalence point, we have some HCl that has reacted with NaOH and some HCl that is still unreacted. Because they have the same concentrations, let's say we add 10.00 mL of NaOH.

NaOH

$n = CV$

$= (0.300M)(0.0100L)$

$= 3 \times 10^{-3}$ mol

$= 3$ mmol

HCl

$n = CV$

$= (0.300M)(0.020L)$

$= 6 \times 10^{-3}$ mol ← you can keep it in moles.

$= 6$ mmol

So 3mmol of NaOH is available to react with the 6 mmol HCl in the solution. Therefore looking at the mole to mole ratios, there would be 3mmol of OH^- and 6mmol of H^+ present.

So, if 3 mmol of OH^- and 6mmol of H^+, there would be 3mmol of H^+ remaining.

So, $[H^+] = n/V$

$$= \frac{3 \times 10^{-3} \text{ mol}}{0.03 \text{ L}} \longrightarrow V_T = 20 \text{ mL HCl} + 20 \text{ mL of NaOH}$$

$$= 0.100 \text{ M}$$

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

$$= -\log(0.100)$$

$$= 1.000$$

This makes sense as we have added some base to make the acidic solution more basic.

c) At Equivalence Point – 20.00 mL NaOH (neutralization)

At equivalence point, we must have an equal number of moles of HCl reacting with NaOH.

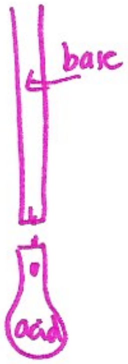
So we would need to add 20.00 mL of NaOH to produce the same 6.00 mmol of NaOH to completely react with the 6.00 mmol of HCl. Therefore all that is left in the solution would be water.

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

$$= -\log(1 \times 10^{-7} \text{ M})$$

$$= 7.00$$

Therefore in any strong acid-strong base titration, the pH will always be 7 at the equivalence point. !!!



d) After the Equivalence Point – 30.00 mL of NaOH

Once we are past the equivalence point, there is only NaOH present and no HCl present.

NaOH

$$n = C \times V_T$$
$$= (0.300M)(0.03L)$$
$$= 9 \times 10^{-3} \text{mol}$$
$$= 9 \text{mmol}$$

So we know that 6.00 mmol of NaOH already reacted with HCl so there is only 3 mmol of NaOH left unreacted.

So, $[OH^-] = n/V_T$
$$= \frac{3 \times 10^{-3} \text{mol}}{0.05L}$$
$$= 0.06 \frac{\text{mol}}{L}$$

And, pOH = -log[OH]
$$= -\log(0.06)$$
$$= 1.22$$

$$pH = 14.00 - pOH$$
$$= 14.00 - 1.22 = 12.80$$

This makes sense as we only have base left in the solution.

Indicators

pKa = -log Ka

In order to determine an appropriate indicator, we must choose one that has a pKa value that falls within the pH range of the titration solution at equivalence point. Some common indicator values can be found on pg. 609 of your textbook.

So if we look at our previous examples:

Titrating 20.00 mL of a 0.300 mol/L $HCl_{(aq)}$ solution with a 0.300 mol/L $NaOH_{(aq)}$ solution gave us a pH of 7 at equivalence point. An appropriate indicator could be bromothymol blue

Titrating 20.00 mL of a 0.300 mol/L $HC_2H_3O_{2(aq)}$ solution with a 0.300 mol/L $NaOH_{(aq)}$ solution gave us a pH of 8.97 at equivalence point. An appropriate indicator could be thymol blue.

Buffers

Buffers are a mixture of a weak conjugate acid-base solution. The importance of a buffer is that it has the unique ability to maintain its pH with little to no change even with the addition of a strong acid or base

Review Questions

Homework: pg. 547 #1,2, ~~pg.554 #1-2,~~ pg.557 ~~#1-8~~, pg.565 #1-3,pg.567 #1-8 | pg.575 #1-21, pg.576 #1-80

↳ #1,2

Read section 8.8