

## Unit 8 REVIEW

### Part 1

(Pages 774–775)

1. B
2. A
3. C
4. A
5. A
6. B
7. A
8. A
9. 3, 6, 1, and 1
10. C
11. A
12. C
13. A
14. D

### Solutions

9. For any weak acid, HA(aq), at equilibrium:  $\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$

$$[\text{A}^-(\text{aq})] = [\text{H}_3\text{O}^+(\text{aq})] = 10^{-\text{pH}} = 10^{-5.22} = 6.0 \times 10^{-6} \text{ mol/L}$$

$$[\text{HA(aq)}] = (1.00 - 6.0 \times 10^{-6}) = 1.00 \text{ mol/L}$$

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA(aq)}]} = \frac{[6.0 \times 10^{-6}]^2}{[1.00]} = 3.6 \times 10^{-11}$$

### Part 2

(Pages 775–779)

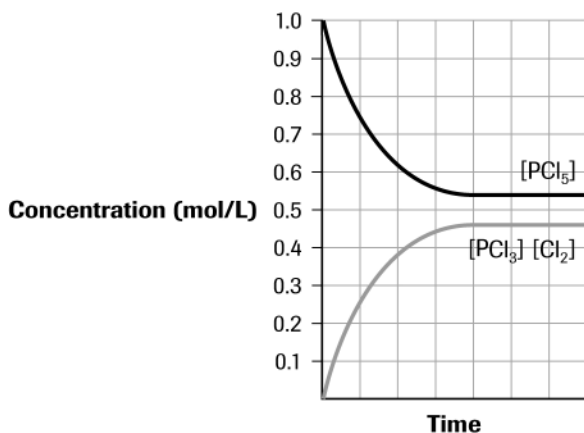
15. According to the oxygen concept, all acids contain oxygen. This definition is too restricted and has too many exceptions, notably HCl(aq). According to the hydrogen concept, all acids are compounds of hydrogen. This definition is limited because it does not explain why only certain hydrogen compounds are acids. According to Arrhenius' concept, acids are substances that ionize in aqueous solution to produce hydrogen ions. This definition is limited to aqueous solutions and cannot explain or predict the properties of many common substances. According to the Brønsted–Lowry concept, acids are substances that donate protons to bases in a chemical reaction. The main limitation of the Brønsted–Lowry concept is the restriction to protons and the inability to explain and predict the acid nature of ions of multi-valent metals.
16. The theory is restricted, revised, or replaced.
17. Test the explanations and predictions made using the theory.
18. According to the evidence, the hydrogen ion exists as a hydrated proton whose simplest representation is the hydronium ion,  $\text{H}_3\text{O}^+(\text{aq})$ .
19. According to Arrhenius' concept, a base is a substance that dissociates in aqueous solution to produce hydroxide ions. According to the revised Arrhenius concept, a base is a substance that reacts with water to produce hydroxide ions. According to the Brønsted–Lowry concept, a base is a proton acceptor that removes protons from an acid.
20. Both sodium sulfite and sodium carbonate would make basic solutions, as sulfite ion and carbonate ion are proton acceptors. A check of the Relative Strengths of Acids and Bases

table (Appendix I) shows that carbonate ion is lower on the basic side of the table than sulfite ion. This means that a solution of carbonate ion would be more basic than a sulfite ion solution of the same concentration.

21. If a pH meter is used to test both a sodium hydroxide solution and a sodium benzoate solution, *and* the pH of one of the solutions is much lower than the other, *then* the solution with the lower pH will be sodium hydroxide.  
or  
If a conducting apparatus is used to test each solution, *and* one solution conducted better than the other, *then* the solution that conducted better is the stronger base, sodium hydroxide.
22. The two conjugate acid–base pairs would be:  $\text{H}_2\text{PO}_4^- (\text{aq}) - \text{HPO}_4^{2-} (\text{aq})$ , and  $\text{H}_3\text{PO}_4 (\text{aq}) - \text{H}_2\text{PO}_4^- (\text{aq})$ .
23. (a) False—The stronger base is a reactant.  
(b) True—The equilibrium constant is likely greater than one.  
(c) True—The forward reaction is exothermic. (based on the generalization that a–b neutralizations are generally exothermic)  
(d) True—The stronger acid is a reactant.  
(e) True—The percent reaction is greater than 50%.  
(f) True—The pH of the final solution is likely greater than 7.  
(g) True—The reactant acid is above the reactant base in an acid–base table.
24. (a) The system changes that could shift the equilibria towards propene would be: increased temperature, addition of propane, removal of propene, removal of hydrogen, and a decrease in overall pressure.  
(b) The system changes that could shift the equilibria towards iodine would be: addition of tin(II) ion, addition of iodate ion, decrease in pH (addition of hydronium ion), and the removal of iodine and/or tin(IV) ion.
25. (a) ICE Table for  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

Concentration	$[\text{PCl}_5(\text{g})]$ (mol/L)	$[\text{PCl}_3(\text{g})]$ (mol/L)	$[\text{Cl}_2(\text{g})]$ (mol/L)
Initial	1.0	0	0
Change	-0.46	+0.46	+0.46
Equilibrium	0.54	0.46	0.46

(Alternatively,  $K_c$  expression and value could be used.)

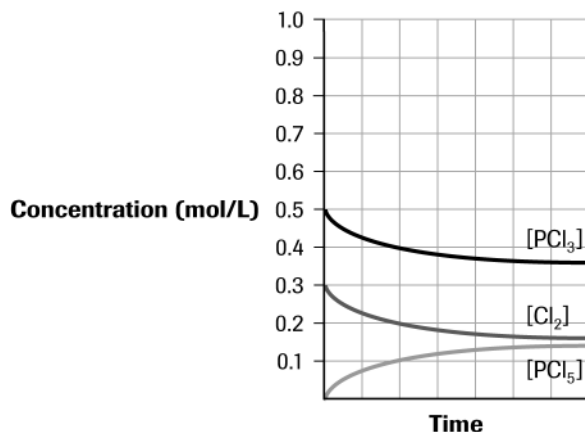


The concentrations of  $\text{PCl}_3$  and  $\text{Cl}_2$  both begin at zero, increase, and level off at 0.46 mol/L.

(b) ICE Table for  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

Concentration	$[\text{PCl}_5(\text{g})]$ (mol/L)	$[\text{PCl}_3(\text{g})]$ (mol/L)	$[\text{Cl}_2(\text{g})]$ (mol/L)
Initial	0	0.50	0.30
Change	+0.14	-0.14	-0.14
Equilibrium	0.14	0.36	0.16

(Alternatively,  $K_c$  expression and value could be used.)



The 0.30 mol/L initial concentration of  $\text{Cl}_2$  decreases by 0.14 mol/L, to 0.16 mol/L at equilibrium.

The zero initial concentration of  $\text{PCl}_5$  increases by 0.14 mol/L, to 0.14 mol/L at equilibrium.

26. The initial concentration for each chemical is 1.00 mol/L (1.00 mol in a 1.00 L volume). Assume the reaction shifts right to reach equilibrium, and let  $x$  equal the decrease in  $[\text{CO}(\text{g})]$ . (Note that if the assumption is wrong and the reaction shifts left, the value of  $x$  will still be correct, but it will be a negative value, because it would then represent a negative decrease—that is, an increase.)

ICE Table for  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$   $K_c = 5.0$  at  $650^\circ\text{C}$

Concentration	$[\text{CO}(\text{g})]$ (mol/L)	$[\text{H}_2\text{O}(\text{g})]$ (mol/L)	$[\text{CO}_2(\text{g})]$ (mol/L)	$[\text{H}_2(\text{g})]$ (mol/L)
Initial	1.00	1.00	1.00	1.00
Change	- $x$	- $x$	+ $x$	+ $x$
Equilibrium	$1.00 - x$	$1.00 - x$	$1.00 + x$	$1.00 + x$

$$K_c = \frac{[\text{CO}_2(\text{g})][\text{H}_2(\text{g})]}{[\text{CO}(\text{g})][\text{H}_2\text{O}(\text{g})]}$$

$$5.0 = \frac{(1.00 + x)^2}{(1.00 - x)^2} \text{ and taking the square root of both sides}$$

$$\sqrt{5.0} = \sqrt{\frac{(1.00 + x)^2}{(1.00 - x)^2}} = \frac{1.00 + x}{1.00 - x} \text{ and multiplying both sides by } 1.00 - x$$

$$\sqrt{5.0} - \sqrt{5.0} x = 1.00 + x \text{ and solving for } x:$$

$x = 0.38$  and since this value is positive, the reaction has shifted right to establish equilibrium, as originally assumed.

Therefore, at equilibrium,

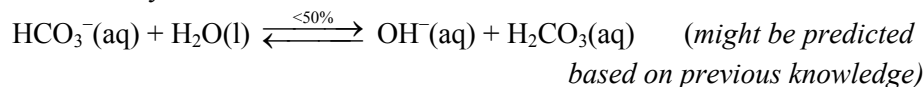
$$[\text{CO}(\text{g})] = [\text{H}_2\text{O}(\text{g})] = (1.00 - x) \text{ mol/L} = (1.00 - 0.38) \text{ mol/L} = 0.62 \text{ mol/L}$$

$$[\text{CO}_2(\text{g})] = [\text{H}_2(\text{g})] = (1.00 + x) \text{ mol/L} = (1.00 + 0.38) \text{ mol/L} = 1.38 \text{ mol/L}$$





ion are possible: either hydrogen carbonate ion reacts predominantly as an acid, or else it reacts predominantly as a base.



or 
$$\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{<50\%} \text{H}_3\text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$$
  
(The five-step method, by itself, does not allow prediction of which reaction will predominate.)

If the pH is tested, and increases upon dissolving the sodium hydrogen carbonate, then the aqueous hydrogen carbonate ions have predominantly reacted to produce hydroxide ions as predicted by the first equation.

If the pH is tested, and decreases upon dissolving the sodium hydrogen carbonate, then the aqueous hydrogen carbonate ions have predominantly reacted to produce hydronium ions as predicted by the second equation.

31. According to Le Châtelier's principle, the equilibrium will shift as follows:

(1) Increasing  $[\text{OH}^-(\text{aq})]$  should shift the equilibrium left.

An ammonia odour should be detectable, and should also be stronger than before the addition.

(2) Increasing  $[\text{OH}^-(\text{aq})]$  should cause a quantitative reaction with the hydronium ions, decreasing  $[\text{H}_3\text{O}^+(\text{aq})]$  and shifting the equilibrium right.

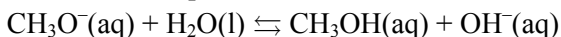
The colour of the solution should turn blue or stay blue.

(3) Increasing  $[\text{OH}^-(\text{aq})]$  should cause a quantitative reaction with the hydronium ions, decreasing  $[\text{H}_3\text{O}^+(\text{aq})]$  and shifting the equilibrium right.

A vinegar odour should no longer be detectable, or should be much reduced in intensity.

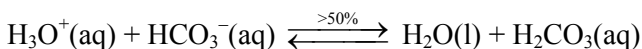
Le Châtelier's principle is able to provide a specific prediction in each case.

32. The solution is predicted to be basic.



Water can act as an acid or base, but the methoxide ion can only act as a base because that is the only logical possibility judging from the product.  $\text{CH}_3\text{OH}$  is a known substance,  $\text{CH}_2\text{O}^{2-}$  is not a known substance.

33. 
$$\text{OH}^-(\text{aq}) + \text{HCO}_3^-(\text{aq}) \xrightleftharpoons{>50\%} \text{H}_2\text{O}(\text{l}) + \text{CO}_3^{2-}(\text{aq})$$



The amphiprotic entity is the  $\text{HCO}_3^-(\text{aq})$  ion. Sodium bicarbonate is an amphoteric substance, that is capable of reacting in order to "consume" most of either a strong acid or a strong base.

34. If the solutions are tested with a pH meter, and the pH values are ordered from smallest to largest, then the solutions are sulfuric acid, hydrochloric acid, acetic acid, ethane-1,2-diol, ammonia, sodium hydroxide, and barium hydroxide, respectively, using acid and base strengths to order the substances. The ethane-1,2-diol solution is assumed to be neutral. For equal concentrations, a sulfuric acid solution will have a lower pH than a hydrochloric acid solution, because of secondary (extra) ionization of hydrogen sulfate ions. Also, for equal concentrations, a barium hydroxide solution will have a higher pH than a sodium hydroxide solution, because dissociation upon dissolving produces twice as many hydroxide ions.

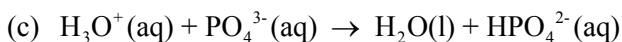
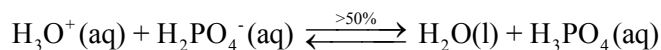
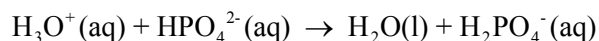
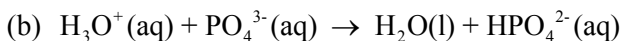
The solutions may also be tested for relative conductivity, and for acidity or basicity by testing for colour changes with both red and blue litmus paper, and for the relative volume of titrant needed for titration to a (final) equivalence point.

## Diagnostic Tests on the Unlabelled Solutions

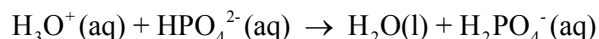
Litmus	Conductivity*	Acid/base titration	Analysis
blue to red	low	one volume	CH <sub>3</sub> COOH(aq)
red to blue	higher	two volumes	Ba(OH) <sub>2</sub> (aq)
red to blue	low	one volume	NH <sub>3</sub> (aq)
no changes	none	not applicable	C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub> (aq)
blue to red	higher	two volumes	H <sub>2</sub> SO <sub>4</sub> (aq)
blue to red	high	one volume	HCl(aq)
red to blue	high	one volume	NaOH(aq)

\* relative conductivity of the acidic or basic solutions

35. (a) There are two quantitative reactions as there are two rapid decreases in pH during the titration.



At 1<sup>st</sup> equivalence point:  $V_{\text{H}_3\text{O}^+} \cong 25 \text{ mL}$  (read from the pH curve)



At 2<sup>nd</sup> equivalence point:  $V_{\text{H}_3\text{O}^+} \cong 50 \text{ mL}$  (read from the pH curve)

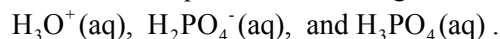
- (d) At 1<sup>st</sup> equivalence point: thymol blue (8.0 - 9.6)

At 2<sup>nd</sup> equivalence point: methyl orange (3.2 - 4.4)

- (e) The first buffering region is before the first endpoint at pH 9. The entities present (other than water) are:  $\text{PO}_4^{3-}(\text{aq})$  and  $\text{HPO}_4^{2-}(\text{aq})$ .

The second buffering region is after the first endpoint and before the second endpoint at pH 4. The entities present (other than water) are:  $\text{HPO}_4^{2-}(\text{aq})$  and  $\text{H}_2\text{PO}_4^-(\text{aq})$ .

After the second endpoint is a third buffering region, created because the third reaction is not quantitative. During this final area the entities present (other than water) are:



36. ICE Table for  $\text{H}_2\text{O}(\text{g}) + \text{Cl}_2\text{O}(\text{g}) \rightleftharpoons 2 \text{HOCl}(\text{g})$   $K_c = 0.090$  at 25 °C

Concentration	[H <sub>2</sub> O(g)] (mol/L)	[Cl <sub>2</sub> O(g)] (mol/L)	[HOCl(g)] (mol/L)
Initial	4.00	4.00	0
Change	- x	- x	+2 x
Equilibrium	4.00 - x	4.00 - x	2 x

$$K_c = \frac{[\text{HOCl}(\text{g})]^2}{[\text{H}_2\text{O}(\text{g})][\text{Cl}_2\text{O}(\text{g})]}, \text{ so } 0.090 = \frac{(2x)^2}{(4.00 - x)^2}$$

$$\sqrt{0.090} = \sqrt{\frac{(2x)^2}{(4.00 - x)^2}}$$

$$0.30 = \frac{2x}{4.00 - x}$$

$$1.2 - 0.30x = 2x \text{ and, solving for } x$$

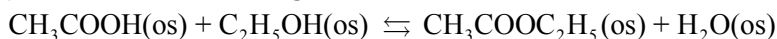
$$x = 0.52$$

At equilibrium:

$$[\text{H}_2\text{O}(\text{g})] = [\text{Cl}_2\text{O}(\text{g})] = (4.00 - x) \text{ mol/L} = (4.00 - 0.52) \text{ mol/L} = 3.48 \text{ mol/L}$$

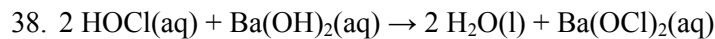
$$[\text{HOCl}(\text{g})] = 2x = 2(0.52 \text{ mol/L}) = 1.04 \text{ mol/L}$$

37. (Note that water is a reagent in solution—with variable concentration—in this reaction.)



$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5(\text{os})][\text{H}_2\text{O}(\text{os})]}{[\text{CH}_3\text{COOH}(\text{os})][\text{C}_2\text{H}_5\text{OH}(\text{os})]} = \frac{(3.1)(3.1)}{(2.5)(1.7)} = 2.3$$

Using the evidence provided and the equilibrium law expression, the equilibrium constant for the reaction at 25 °C is 2.3.



10.0 mL      12.6 mL

*c*              0.350 mol/L

$$n_{\text{Ba}(\text{OH})_2} = 12.6 \text{ mL} \times \frac{0.350 \text{ mol}}{1 \text{ L}} = 4.41 \text{ mmol}$$

$$n_{\text{HOCl}} = 4.41 \text{ mmol} \times \frac{2}{1} = 8.82 \text{ mmol}$$

$$[\text{HOCl}(\text{aq})] = \frac{8.82 \text{ mmol}}{10.0 \text{ mL}} = 0.882 \text{ mol/L}$$

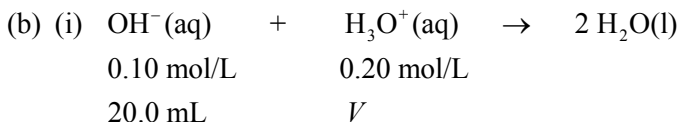
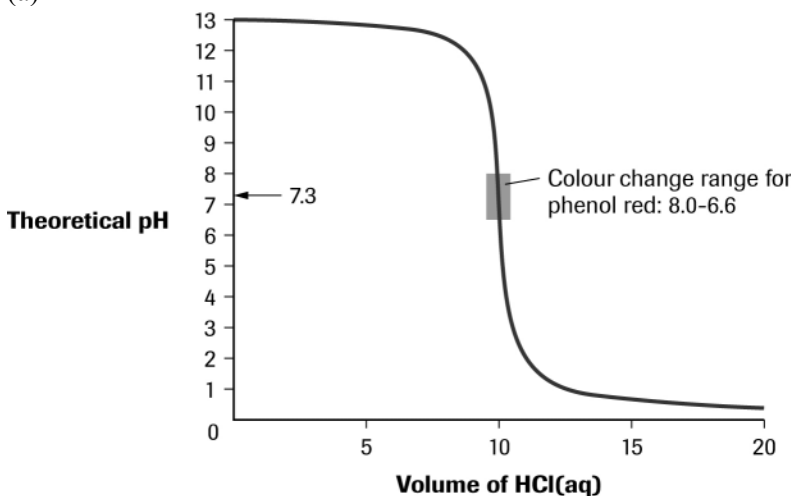
or

$$[\text{HOCl}(\text{aq})] = 12.6 \text{ mL Ba}(\text{OH})_2 \times \frac{0.350 \text{ mol Ba}(\text{OH})_2}{1 \text{ L Ba}(\text{OH})_2} \times \frac{2 \text{ mol HOCl}}{1 \text{ mol Ba}(\text{OH})_2} \times \frac{1}{10.0 \text{ mL HOCl}}$$

$$= 0.882 \text{ mol/L HOCl}$$

According to the evidence, the amount concentration of the acid solution is predicted to be 0.882 mol/L.

39. (a)



The pH at this reaction's equivalence point is assumed to be 7.00, because this is a strong acid–strong base reaction. At the equivalence point, the titrant volume added is:

$$n_{\text{OH}^-} = 20.0 \text{ mL} \times \frac{0.10 \text{ mol}}{1 \text{ L}} = 2.0 \text{ mmol}$$

$$n_{\text{H}_3\text{O}^+} = 2.0 \text{ mmol} \times \frac{1}{1} = 2.0 \text{ mmol}$$

$$V_{\text{H}_3\text{O}^+} = 2.0 \text{ mmol} \times \frac{1 \text{ L}}{0.20 \text{ mol}} = 10 \text{ mL}$$

According to the balanced reaction equation and the rules of stoichiometry, therefore, the volume of titrant at the equivalence point is 10 mL.

(ii)  $\text{pOH} = -\log [\text{OH}^- (\text{aq})] = -\log(0.10) = 1.00$

$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.00 = 13.00$



$$n_{\text{OH}^-} = 20.0 \text{ mL} \times \frac{0.10 \text{ mol}}{1 \text{ L}} = 2.0 \text{ mmol}$$

$$n_{\text{H}_3\text{O}^+} = 5.0 \text{ mL} \times \frac{0.20 \text{ mol}}{1 \text{ L}} = 1.0 \text{ mmol}$$

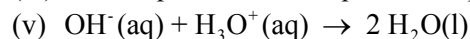
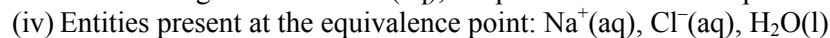
Because the reacting ratio is 1:1,  $\text{OH}^- (\text{aq})$  is in excess, by  $(2.0 - 1.0) \text{ mmol} = 1.0 \text{ mmol}$

$$[\text{OH}^- (\text{aq})] = \frac{n}{V} = \frac{1.0 \text{ mmol}}{(20.0 + 5.0) \text{ mL}} = 0.040 \text{ mol/L}$$

$\text{pOH} = -\log [\text{OH}^- (\text{aq})] = -\log(0.040) = 1.40$

$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.40 = 12.60$

After adding 5.0 mL of  $\text{HCl}(\text{aq})$ , the pH of the solution is predicted to be 12.60.



$$n_{\text{OH}^-} = 20.0 \text{ mL} \times \frac{0.10 \text{ mol}}{1 \text{ L}} = 2.0 \text{ mmol}$$

$$n_{\text{H}_3\text{O}^+} = 9.0 \text{ mL} \times \frac{0.20 \text{ mol}}{1 \text{ L}} = 1.8 \text{ mmol}$$

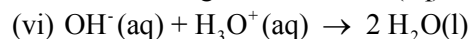
Because the reacting ratio is 1:1,  $\text{OH}^- (\text{aq})$  is in excess, by  $(2.0 - 1.8) \text{ mmol} = 0.2 \text{ mmol}$

$$[\text{OH}^- (\text{aq})] = \frac{n}{V} = \frac{0.2 \text{ mmol}}{(20.0 + 9.0) \text{ mL}} = 0.007 \text{ mol/L}$$

$\text{pOH} = -\log [\text{OH}^- (\text{aq})] = -\log(0.007) = 2.2$

$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.2 = 11.8$

After adding 9.0 mL of  $\text{HCl}(\text{aq})$ , the pH of the solution is predicted to be 11.8.



$$n_{\text{OH}^-} = 20.0 \text{ mL} \times \frac{0.10 \text{ mol}}{1 \text{ L}} = 2.0 \text{ mmol}$$

$$n_{\text{H}_3\text{O}^+} = 11.0 \text{ mL} \times \frac{0.20 \text{ mol}}{1 \text{ L}} = 2.2 \text{ mmol}$$

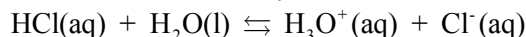
Because the reacting ratio is 1:1,  $\text{H}_3\text{O}^+(\text{aq})$  is in excess, by  $(2.2 - 2.0) \text{ mmol} = 0.2 \text{ mmol}$

$$[\text{H}_3\text{O}^+(\text{aq})] = \frac{n}{V} = \frac{0.2 \text{ mmol}}{(20.0 + 11.0) \text{ mL}} = 0.006 \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+(\text{aq})] = -\log(0.006) = 2.2$$

After adding 11.0 mL of  $\text{HCl}(\text{aq})$ , the pH of the solution is predicted to be 2.2.

- (c) A suitable indicator is bromothymol blue (6.0-7.6). (*Several other indicators such as litmus would also be appropriate.*)
40. (a) Since the  $K$  value (0.000 001 3) is very much less than 1, the solubility equilibrium greatly favours the solid (undissolved) substance. Therefore, calcium hydroxide has a very low solubility.
- (b) A saturated solution of calcium hydroxide (slaked lime) is called limewater. Limewater tests for the presence of carbon dioxide by turning a milky white when exposed to it.
- (c) Calcium hydroxide is a relatively safe base to handle, even though it contains hydroxide ion, because it has a very low solubility in water and cannot form solutions with a very high pH. Even a saturated solution does not contain a very high concentration of hydroxide ions, so is not particularly dangerous if it comes into contact with skin. (*However, any basic solution is a serious problem if it does contact the eyes.*)
- (d) “Liming” soil raises the pH only slightly because calcium hydroxide is only slightly soluble, and so it releases only a small amount of hydroxide ions before reaching solubility equilibrium. It can keep the soil at a slightly elevated pH for a long time, because as hydronium ions in the soil consume the free hydroxide ions, the equilibrium will gradually shift to the right, slowly dissociating more calcium hydroxide and producing more hydroxide ions.
41. Assuming a full, sealed bottle of concentrated hydrochloric acid, the main equilibrium is:



If one out of every four molecules present is  $\text{HCl}$ , then this equilibrium cannot be quantitative (>99%), as would be the case for strong acids in dilute solutions. If we interpret “one out of every four molecules” to mean that three out of the four have reacted, then the fraction of molecules that have reacted is 75%.

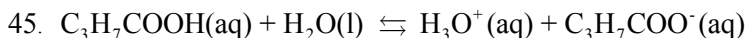
42. When neutralizing a strong acid spill with calcium hydroxide, the calcium hydroxide should be in excess. Having the calcium hydroxide in excess means that the more dangerous aqueous hydronium ions are removed from the environment, leaving the much less dangerous solid calcium hydroxide. Calcium can only form weakly basic solutions because of its very low solubility, and therefore it would not affect the environment as much.
43. Chemical equation:  $\text{Ca}(\text{OH})_2(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$   
 Brønsted–Lowry equation:  $\text{OH}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$

44. (a)

Acids	Bases	Conjugate acid/base pair
$\text{C}_4\text{H}_4\text{NH}$ , $(\text{C}_6\text{H}_5)_3\text{CH}$	$(\text{C}_6\text{H}_5)_3\text{C}^-$ , $\text{C}_4\text{H}_4\text{N}^-$	$\text{C}_4\text{H}_4\text{NH}/\text{C}_4\text{H}_4\text{N}^-$ $(\text{C}_6\text{H}_5)_3\text{CH}/(\text{C}_6\text{H}_5)_3\text{C}^-$
$\text{CH}_3\text{COOH}$ , $\text{H}_2\text{S}$	$\text{HS}^-$ , $\text{CH}_3\text{COO}^-$	$\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ $\text{H}_2\text{S}/\text{HS}^-$
$(\text{C}_6\text{H}_5)_3\text{CH}$ , $\text{OH}^-$	$\text{O}^{2-}$ , $(\text{C}_6\text{H}_5)_3\text{C}^-$	$(\text{C}_6\text{H}_5)_3\text{CH}/(\text{C}_6\text{H}_5)_3\text{C}^-$ $\text{OH}^-/\text{O}^{2-}$
$\text{H}_2\text{S}$ , $\text{C}_4\text{H}_4\text{NH}$	$\text{C}_4\text{H}_4\text{N}^-$ , $\text{HS}^-$	$\text{H}_2\text{S}/\text{HS}^-$ $\text{C}_4\text{H}_4\text{NH}/\text{C}_4\text{H}_4\text{N}^-$

- (b)

Acid	Conjugate base
$\text{CH}_3\text{COOH}$	$\text{CH}_3\text{COO}^-$
$\text{H}_2\text{S}$	$\text{HS}^-$
$\text{C}_4\text{H}_4\text{NH}$	$\text{C}_4\text{H}_4\text{N}^-$
$(\text{C}_6\text{H}_5)_3\text{CH}$	$(\text{C}_6\text{H}_5)_3\text{C}^-$
$\text{OH}^-$	$\text{O}^{2-}$



At equilibrium,

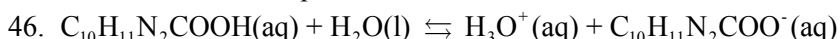
$$[\text{H}_3\text{O}^+(\text{aq})] = [\text{C}_3\text{H}_7\text{COO}^-(\text{aq})] = 0.00124 \text{ mol/L}$$

$$[\text{C}_3\text{H}_7\text{COOH}(\text{aq})] = (0.100 - 0.00124) \text{ mol/L} = 0.099 \text{ mol/L}$$

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{C}_3\text{H}_7\text{COO}^-(\text{aq})]}{[\text{C}_3\text{H}_7\text{COOH}(\text{aq})]} = \frac{(0.00124)^2}{0.099} = 1.6 \times 10^{-5}$$

$$p = \frac{[\text{H}_3\text{O}^+(\text{aq})]}{[\text{C}_3\text{H}_7\text{COOH}(\text{aq})]} \times 100\% = \frac{0.00124 \text{ mol/L}}{0.100 \text{ mol/L}} \times 100\% = 1.24\%$$

According to the evidence provided, and the equilibrium law, the  $K_a$  for *n*-butanoic acid is  $1.6 \times 10^{-5}$ , while the percent reaction is 1.24%.



At equilibrium,

$$[\text{H}_3\text{O}^+(\text{aq})] = [\text{C}_{10}\text{H}_{11}\text{N}_2\text{COO}^-(\text{aq})] = 10^{-\text{pH}} \text{ mol/L} = 10^{-5.19} \text{ mol/L} = 6.5 \times 10^{-6} \text{ mol/L}$$

$$[\text{C}_{10}\text{H}_{11}\text{N}_2\text{COOH}(\text{aq})] = (0.10 - 0.0000065) \text{ mol/L} = 0.10 \text{ mol/L}$$

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{C}_{10}\text{H}_{11}\text{N}_2\text{COO}^-(\text{aq})]}{[\text{C}_{10}\text{H}_{11}\text{N}_2\text{COOH}(\text{aq})]} = \frac{(6.5 \times 10^{-6})^2}{0.10} = 4.2 \times 10^{-10} \text{ mol/L}$$

$$p = \frac{[\text{H}_3\text{O}^+(\text{aq})]}{[\text{C}_{10}\text{H}_{11}\text{N}_2\text{COOH}(\text{aq})]} \times 100\% = \frac{6.5 \times 10^{-6} \text{ mol/L}}{0.10 \text{ mol/L}} \times 100\% = 6.5 \times 10^{-3} \%$$

47. The quadratic formula is not required, as glycine is a weak acid and

$$\frac{[\text{H}_2\text{NCH}_2\text{COOH}(\text{aq})]}{K_a} = \frac{0.050}{4.5 \times 10^{-7}} = 111\,111, \text{ which is greater than } 1000.$$

At equilibrium: Let  $x = [\text{H}_3\text{O}^+(\text{aq})] = [\text{H}_2\text{NCH}_2\text{COO}^-(\text{aq})]$

Then  $[\text{H}_2\text{NCH}_2\text{COOH}(\text{aq})] = (0.050 - x) = 0.050 \text{ mol/L}$  (using the assumption)

(Optional) ICE Table for  $\text{H}_2\text{NCH}_2\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{NCH}_2\text{COO}^-(\text{aq})$

Concentration	$[\text{H}_2\text{NCH}_2\text{COOH}(\text{aq})]$ (mol/L)	$[\text{H}_3\text{O}^+(\text{aq})]$ (mol/L)	$[\text{H}_2\text{NCH}_2\text{COO}^-(\text{aq})]$ (mol/L)
Initial	0.050	0	0
Change	- x	+ x	+ x
Equilibrium	$(0.050 - x) = 0.050$	x	x

$$K_a = 4.5 \times 10^{-7} = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{H}_2\text{NCH}_2\text{COO}^-(\text{aq})]}{[\text{H}_2\text{NCH}_2\text{COOH}(\text{aq})]}$$

$$4.5 \times 10^{-7} = \frac{x^2}{0.050}$$

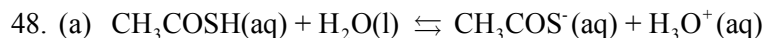
$$x = \sqrt{4.5 \times 10^{-7} \times 0.050} = 1.5 \times 10^{-4}$$

$$[\text{H}_3\text{O}^+(\text{aq})] = 1.5 \times 10^{-4} \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+(\text{aq})] = -\log(1.5 \times 10^{-4}) = 3.82$$

$$p = \frac{[\text{H}_3\text{O}^+(\text{aq})]}{[\text{H}_2\text{NCH}_2\text{COOH}(\text{aq})]} \times 100\% = \frac{1.5 \times 10^{-4} \text{ mol/L}}{0.050 \text{ mol/L}} \times 100\% = 0.30\%$$

According to the equilibrium law, the hydronium ion amount concentration of 0.050 mol/L glycine is, the pH of the solution is 3.82, and the percent reaction is 0.30%.



$$K_a = \frac{[\text{CH}_3\text{COS}^-(\text{aq})][\text{H}_3\text{O}^+(\text{aq})]}{[\text{CH}_3\text{COSH}(\text{aq})]}$$

(b) The quadratic formula is not required, as thioacetic acid is a weak acid and

$$\frac{[\text{CH}_3\text{COSH}(\text{aq})]}{K_a} = \frac{2.00}{4.7 \times 10^{-4}} = 4255, \text{ which is greater than } 1000.$$

At equilibrium: Let  $x = [\text{H}_3\text{O}^+(\text{aq})] = [\text{CH}_3\text{COS}^-(\text{aq})]$

Then  $[\text{CH}_3\text{COSH}(\text{aq})] = (2.00 - x) = 2.00 \text{ mol/L}$  (using the assumption)

(Optional) ICE Table for  $\text{CH}_3\text{COSH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COS}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

Concentration	$[\text{CH}_3\text{COSH}(\text{aq})]$ (mol/L)	$[\text{H}_3\text{O}^+(\text{aq})]$ (mol/L)	$[\text{CH}_3\text{COS}^-(\text{aq})]$ (mol/L)
Initial	2.00	0	0
Change	-x	+x	+x
Equilibrium	$(2.00 - x) = 2.00$	x	x

$$4.7 \times 10^{-4} = \frac{x^2}{2.00}$$

$$x = \sqrt{4.7 \times 10^{-4} \times 2.00} = 3.1 \times 10^{-2}$$

$$[\text{H}_3\text{O}^+(\text{aq})] = [\text{CH}_3\text{COS}^-(\text{aq})] = 3.1 \times 10^{-2} \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+(\text{aq})] = -\log(3.1 \times 10^{-2}) = 1.51$$

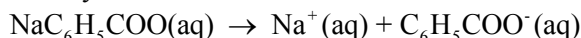
$$p = \frac{[\text{H}_3\text{O}^+(\text{aq})]}{[\text{CH}_3\text{COSH}(\text{aq})]} \times 100\% = \frac{3.1 \times 10^{-2} \text{ mol/L}}{2.00 \text{ mol/L}} \times 100\% = 1.5\%$$

According to the equilibrium law, the hydronium ion and thioacetate ion amount concentrations are both  $3.1 \times 10^{-2} \text{ mol/L}$ , the pH of the solution is 1.51, and the percent reaction is 1.5%, in a 2.00 mol/L solution.

(c) For thioacetate ion:

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{4.7 \times 10^{-4}} = 2.1 \times 10^{-11}$$

49. Initially:



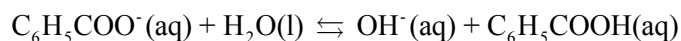
$$[\text{C}_6\text{H}_5\text{COO}^-(\text{aq})] = [\text{NaC}_6\text{H}_5\text{COO}(\text{aq})] = 0.012 \text{ mol/L}$$

(Optional) ICE Table for  $\text{C}_6\text{H}_5\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{C}_6\text{H}_5\text{COOH}(\text{aq})$

Concentration	$[\text{C}_6\text{H}_5\text{COO}^-(\text{aq})]$ (mol/L)	$[\text{OH}^-(\text{aq})]$ (mol/L)	$[\text{C}_6\text{H}_5\text{COOH}(\text{aq})]$ (mol/L)
Initial	0.012	0	0
Change	-x	+x	+x
Equilibrium	$0.012 - x$	x	x

For benzoic acid,  $K_a = 6.3 \times 10^{-5}$

$$\text{For benzoate ion, } K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14} \text{ (mol/L)}^2}{6.3 \times 10^{-5} \text{ mol/L}} = 1.6 \times 10^{-10}$$



At equilibrium:

The quadratic formula is not required, as the base is a weak base and

$$\frac{[\text{C}_6\text{H}_5\text{COO}^-(\text{aq})]}{K_b} = \frac{0.012}{1.6 \times 10^{-10}} = 7.6 \times 10^7, \text{ which is greater than 1000}$$

then,  $[\text{C}_6\text{H}_5\text{COOH}(\text{aq})] = (0.012 - x) = 0.012 \text{ mol/L}$  (using the assumption)

$$K_b = \frac{[\text{OH}^-(\text{aq})][\text{C}_6\text{H}_5\text{COOH}(\text{aq})]}{[\text{C}_6\text{H}_5\text{COO}^-(\text{aq})]}$$

$$1.6 \times 10^{-10} = \frac{x^2}{0.012}$$

$$x = \sqrt{1.6 \times 10^{-10} \times 0.012} = 1.4 \times 10^{-6}$$

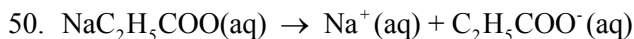
$$[\text{OH}^-(\text{aq})] = 1.4 \times 10^{-6} \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-(\text{aq})] = -\log(1.4 \times 10^{-6}) = 5.86$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.86 = 8.14$$

$$p = \frac{[\text{OH}^-(\text{aq})]}{[\text{C}_6\text{H}_5\text{COO}^-(\text{aq})]} \times 100\% = \frac{1.4 \times 10^{-6} \text{ mol/L}}{0.012 \text{ mol/L}} \times 100\% = 0.012\%$$

According to the  $K_w$  expression and the equilibrium law, the hydroxide ion concentration of the sodium benzoate solution is  $1.4 \times 10^{-6}$ , the pOH is 5.86, the pH is 8.14, and the percent reaction is 0.012%.



$$[\text{C}_2\text{H}_5\text{COO}^-(\text{aq})] = [\text{NaC}_2\text{H}_5\text{COO}(\text{aq})] = 0.100 \text{ mol/L}$$



$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 8.95 = 5.05$$

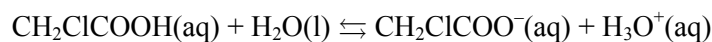
$$[\text{OH}^-(\text{aq})] = [\text{C}_2\text{H}_5\text{COOH}(\text{aq})] = 10^{-\text{pOH}} = 10^{-5.05} = 8.9 \times 10^{-6} \text{ mol/L}$$

$$[\text{C}_2\text{H}_5\text{COO}^-(\text{aq})] = (0.100 - 8.9 \times 10^{-6}) \text{ mol/L} = 0.100 \text{ mol/L}$$

$$K_b = \frac{[\text{OH}^-(\text{aq})][\text{C}_2\text{H}_5\text{COOH}(\text{aq})]}{[\text{C}_2\text{H}_5\text{COO}^-(\text{aq})]} = \frac{(8.9 \times 10^{-6})^2}{0.100} = 7.9 \times 10^{-10}$$

According to the evidence and the equilibrium law, the  $K_b$  for the sodium propanoate solution ion is  $7.9 \times 10^{-10}$ .

51. (a) Chloroacetic acid:

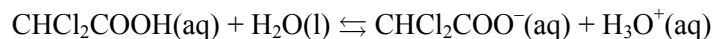


$$[\text{H}_3\text{O}^+(\text{aq})] = [\text{CH}_2\text{ClCOO}^-(\text{aq})] = 10^{-\text{pH}} = 10^{-1.94} = 0.011 \text{ mol/L}$$

$$[\text{CH}_2\text{ClCOOH}(\text{aq})] = (0.100 - 0.011) \text{ mol/L} = 0.089 \text{ mol/L}$$

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{C}_2\text{H}_7\text{COO}^-(\text{aq})]}{[\text{C}_2\text{H}_7\text{COOH}(\text{aq})]} = \frac{(0.011)^2}{0.089} = 1.5 \times 10^{-3}$$

Dichloroacetic acid:

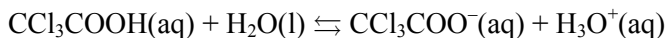


$$[\text{H}_3\text{O}^+(\text{aq})] = [\text{CHCl}_2\text{COO}^-(\text{aq})] = 10^{-\text{pH}} = 10^{-1.30} = 0.050 \text{ mol/L}$$

$$[\text{CHCl}_2\text{COOH}(\text{aq})] = (0.100 - 0.050) \text{ mol/L} = 0.050 \text{ mol/L}$$

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{C}_2\text{H}_7\text{COO}^-(\text{aq})]}{[\text{C}_2\text{H}_7\text{COOH}(\text{aq})]} = \frac{(0.050)^2}{0.050} = 5.0 \times 10^{-2}$$

Trichloroacetic acid:



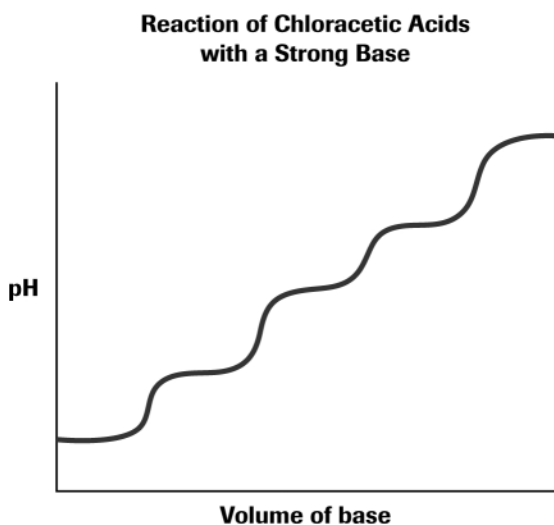
$$[\text{H}_3\text{O}^+(\text{aq})] = [\text{CCl}_3\text{COO}^-(\text{aq})] = 10^{-\text{pH}} = 10^{-1.14} = 0.072 \text{ mol/L}$$

$$[\text{CCl}_3\text{COOH}(\text{aq})] = (0.100 - 0.072) \text{ mol/L} = 0.028 \text{ mol/L}$$

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{C}_3\text{H}_7\text{COO}^-(\text{aq})]}{[\text{C}_3\text{H}_7\text{COOH}(\text{aq})]} = \frac{(0.072)^2}{0.028} = 1.9 \times 10^{-1}$$

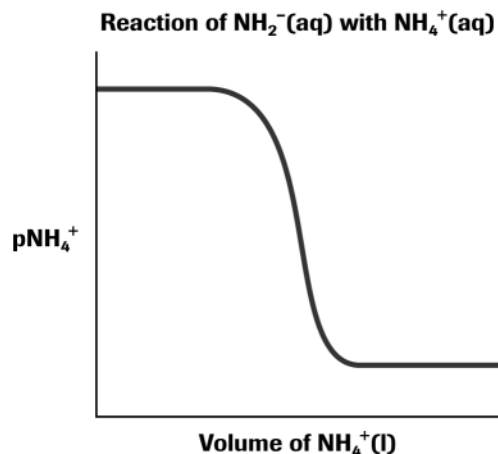
- (b) Evidence indicates that the greater the number of chlorine atoms attached to the first carbon, the stronger an acid the chloroacetic acid becomes. Perhaps because chlorine has a high electronegativity, as the number of chlorine atoms on the first carbon in the molecule increases, other electrons in the molecule are more strongly attracted toward them. As a result, the O–H bond in the COOH group becomes more polar and therefore the O–H bond becomes weaker as that electron pair is pulled away from the proton (H), and toward the oxygen atom. This in turn makes the acid stronger because it is then easier to remove a hydrogen ion (the proton) from the acid molecule.

(c)



The relative amounts of the acids in the mixture can be determined by the relative amounts of base that must be added to get to each successive equivalence point. The more acid present, the more base is required to titrate to the equivalence point of the reaction of the strong base with that acid.

52. (Note: for convenience we can use some simple symbol for showing that entities are “dissolved in the liquid solvent ammonia,” for example, (am) for “ammoniacal,” to parallel the use of “(aq)” in water solutions.)
- The strongest possible acid entity in water solvent is a water molecule with an attached proton,  $\text{H}_3\text{O}^+(\text{aq})$ . The parallel for an ammonia solvent would be for the strongest possible acid entity to be  $\text{NH}_4^+(\text{am})$
  - $\text{NH}_3(\text{l}) + \text{NH}_3(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{am}) + \text{NH}_2^-(\text{am})$
  - The strongest possible base entity in water solvent is a water molecule with a proton removed,  $\text{OH}^-(\text{aq})$ . The parallel for an ammonia solvent would be for the strongest possible base entity to be  $\text{NH}_2^-(\text{am})$
  - It seems logical that value plotted on the vertical axis should be the negative logarithm of the amount concentration of “ammoniacal” ammonium ion,  $\text{NH}_4^+(\text{am})$ , symbolized as  $\text{pNH}_4^+$ , for example.



53. • Chemical systems at equilibrium appear to be static. Observation of properties shows that nothing directly measurable is changing at all, making it appear that no reaction is occurring. However, further examination provides evidence that at a molecular level, at least two reactions are always occurring simultaneously, and they have opposite effects. If each reagent is being produced and consumed at precisely the same rate, then any observed reagent concentration will appear unchanged, at least in any short-term observation. We theorize that chemical equilibrium is always dynamic: it really means that two opposing reactions are occurring, at equal rates.
- Scientists most often predict equilibrium position shifts for a chemical system by applying a generalization (law) called Le Châtelier's principle. This generalization states that the system will always, if possible, shift its equilibrium in the direction that will oppose the initial introduced change. This is theoretically explained by assuming that changing the temperature and/or the concentration of one or more reagents will often have an effect on the rates of (one or both of) the opposing reactions. Whenever the reaction rates are made unequal, we will always observe visible change in the system (shift). Eventually, fluctuating reagent concentrations will reach new values that again make the opposing reaction rates equal, thus establishing a new equilibrium.
  - Acid–base reactions are the most common examples of chemical systems that should always be considered as conditions of equilibrium. When Brønsted–Lowry definitions are applied to acids and bases, they are explained in terms of proton transfer reactions. The transfer of protons between entities is very often not quantitative, therefore understanding the properties of acid–base systems requires applying equilibrium theory. Additionally, the most common solvent used for chemical reactions (water) is a substance that is both an acid and a base according to the Brønsted–Lowry definitions, so the equilibrium of water ionization and the reaction of other acid or base entities with water molecules must also be considered in all acid–base reactions.