7. Equilibrium Concepts and Acid-base Equilibrium

Reversible reactions proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at equilibrium.

Example1: fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Note that a special double arrow is used to emphasize the reversible nature of the reaction.

Cont'd

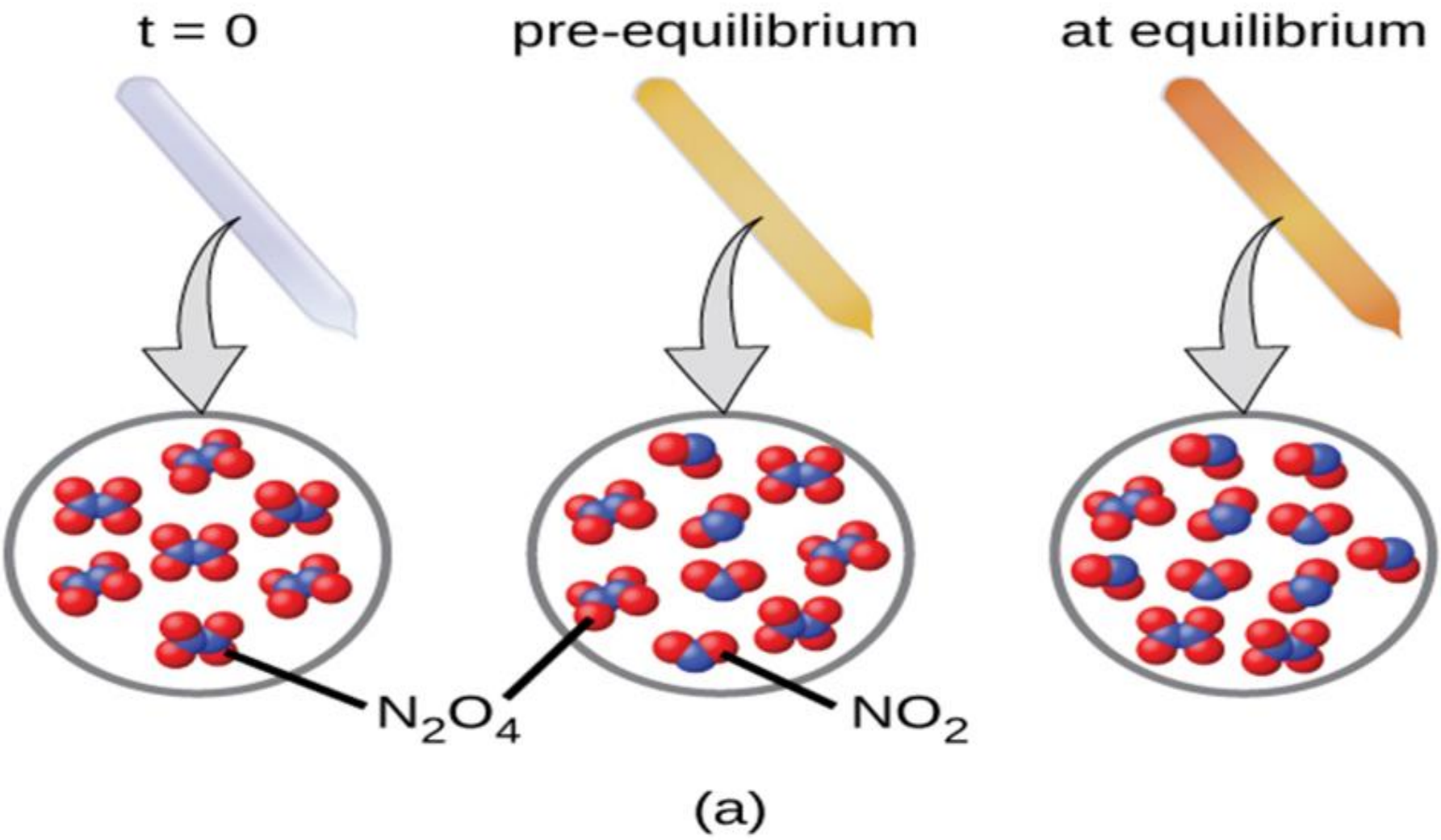


Figure 7.1: (a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2.

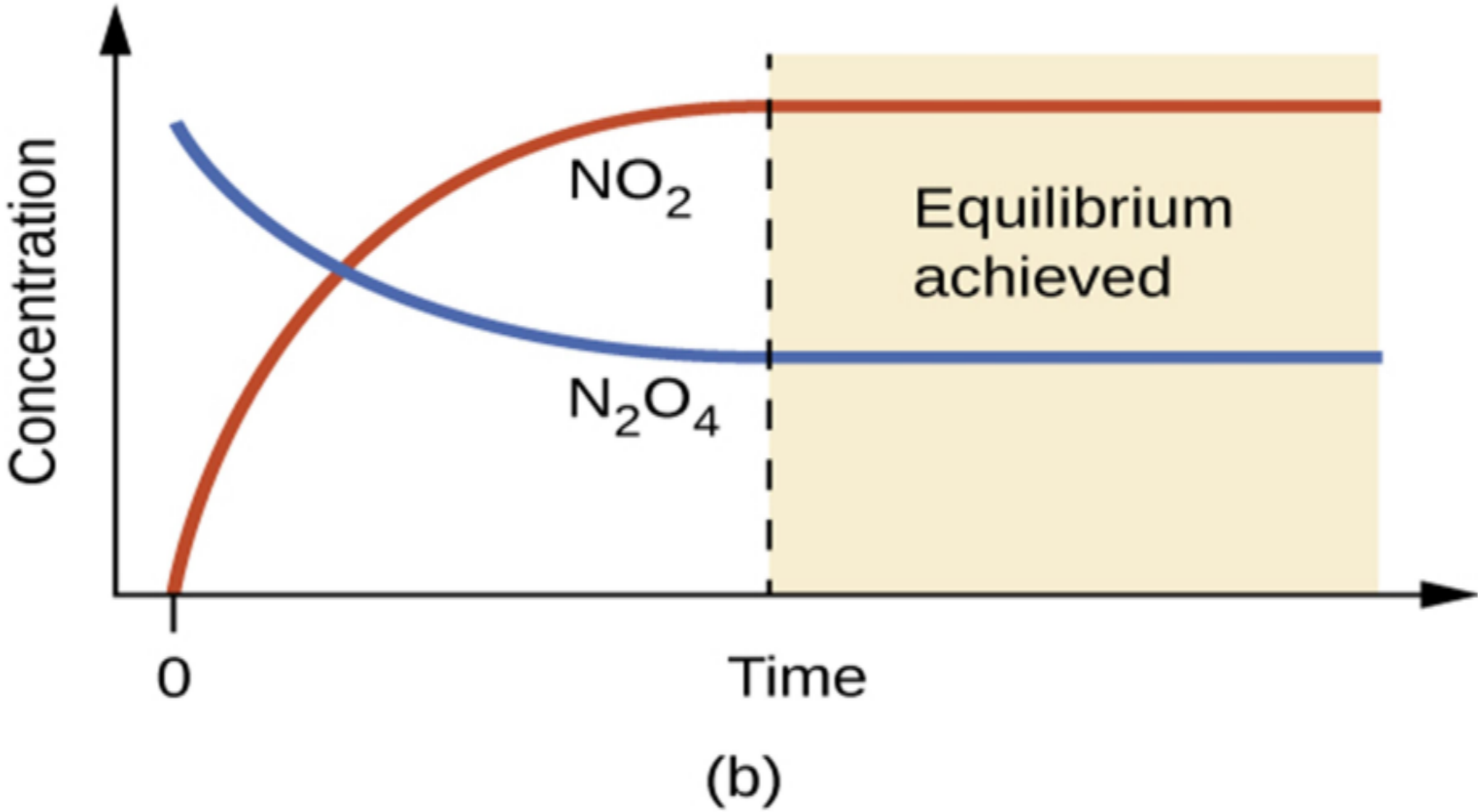


Figure 7.1: (b) Changes in concentration over time as the decomposition reaction achieves equilibrium.

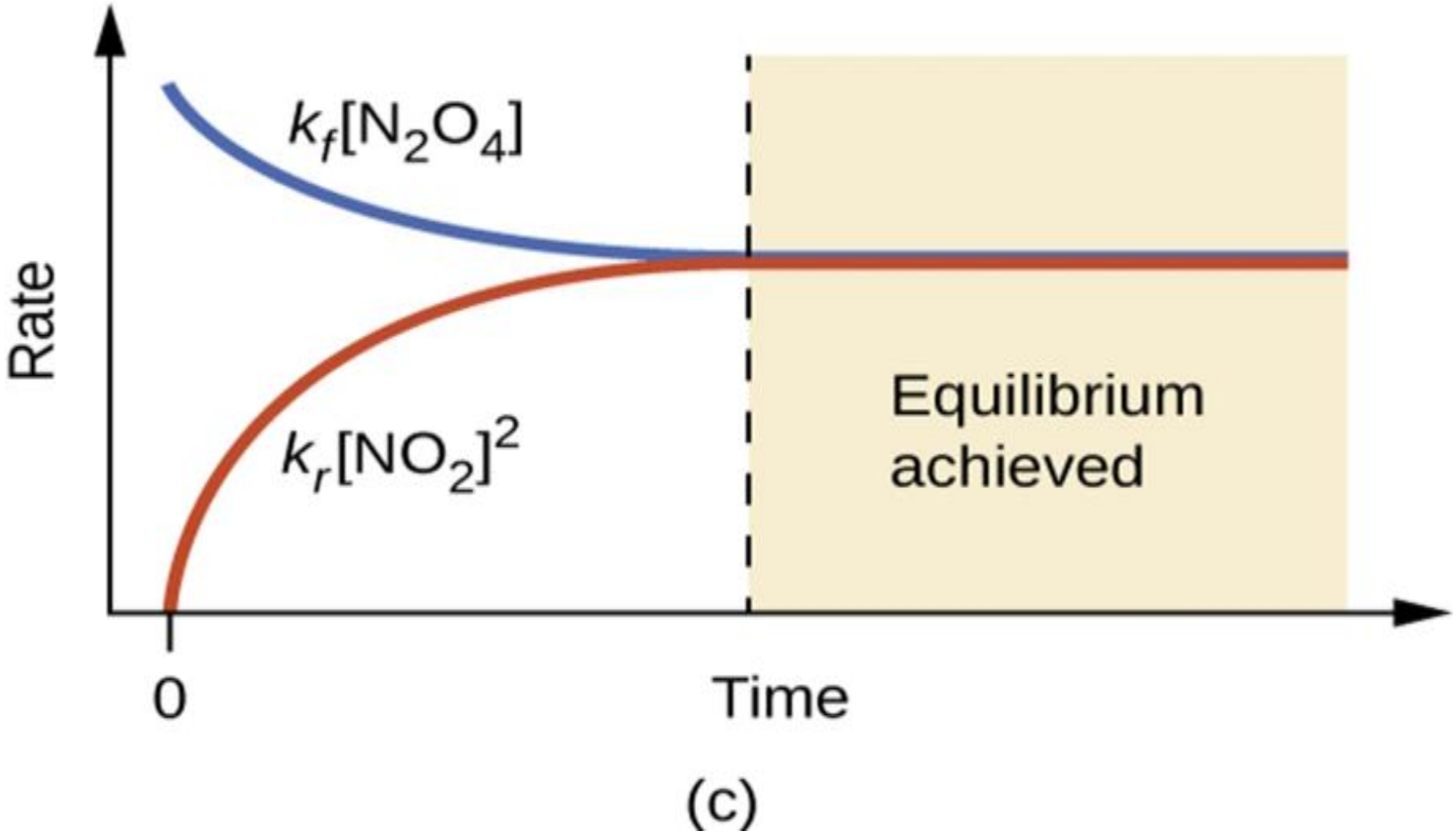


Figure 7.1: (c) At equilibrium, the forward and reverse reaction rates are equal.

Cont'd

- For this elementary process, rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

$$\text{rate}_f = k_f[N_2O_4]$$

$$\text{rate}_r = k_r[NO_2]^2$$

As the reaction begins (t = 0), the concentration of the N_2O_4 reactant is finite and that of the NO_2 product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes, N_2O_4 is consumed and its concentration falls, while NO_2 is produced and its concentration increases (Figure 7.1b). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (Figure 7.1c). This process continues until the forward and reverse reaction rates become equal, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of Figure 7.1b and Figure 7.1c).

Chemical Equilibrium

The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient (*Q*).** For a reversible reaction described by

$$mA + nB + \rightleftharpoons xC + yD$$

The reaction quotient is derived directly from the stoichiometry of the balanced equation as

$$Qc = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

Where, the subscript *c* denotes the use of molar concentrations in the expression. If the reactants and products are gaseous, a reaction quotient may be similarly derived using partial pressures:

$$Qp = \frac{P_C^x P_D^y}{P_A^m P_B^n}$$

Example 7.1 : Writing Reaction Quotient Expressions

- Write the concentration-based reaction quotient expression for each of the following reactions:

a) $3O_2(g) \rightleftharpoons 2O_3(g)$

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

c) $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$

Solution

(a) $Qc = \frac{[O_3]^2}{[O_2]^3}$

(b) $Qc = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(c) $Q_C = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

Example 7.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$\boldsymbol{2NO2(g) \rightleftharpoons N2O4(g)}$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25°C, the concentration changes so that at equilibrium, $[NO_2] = 0.016\ M$ and $[N_2O_4] = 0.042\ M$.

a. What is the value of the reaction quotient before any reaction occurs?

b. What is the value of the equilibrium constant for the reaction?

Solution As for all equilibrium calculations in this text, use the simplified equations for Q and K and disregard any concentration or pressure units, as noted previously in this section.

(a) Before any product is formed, $[NO_2] = \frac{\boldsymbol{0.10mol}}{\boldsymbol{1.0L}} = 0.10M$, and $[N_2O_4] = 0\ M$. Thus,

$$\frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium, $Kc = Qc = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.42}{0.016^2} = 1.6X10^2$. The equilibrium constant is 1.6×10^2.

Home Work

For the reaction

$2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$, the concentrations at equilibrium are $[SO_2] = 0.90\ M$, $[O_2] = 0.35\ M$, and $[SO_3] = 1.1\ M$. What is the value of the equilibrium constant, K_c?

Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving in this reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$$K_C = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.020 *M*	0.011 *M*	0.0094 *M*
$[H_2O]_i$	0.020 *M*	0.0011 *M*	0.0025 *M*
$[CO_2]_i$	0.0040 *M*	0.037 *M*	0.0015 *M*
$[H_2]_i$	0.0040 *M*	0.046 *M*	0.0076 *M*

Solution

Experiment 1:

$$Q_C = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.004)(0.004)}{(0.02)(0.02)} = 0.04$$

$$Qc < Kc\ (0.040 < 0.64)$$

The reaction will proceed in the forward direction.

Experiment 2:

$$Q_C = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4X10^2$$

$$Qc > Kc\ (140 > 0.64)$$

The reaction will proceed in the reverse direction.

Experiment 3:

$$Q_C = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0015)(0.00.0076)}{(0.0094)(0.000.0025)} = 0.48$$

$$Qc < Kc\ (0.48 < 0.64)$$

The reaction will proceed in the forward direction.

Homogeneous Equilibria

A homogeneous equilibrium is one in which all reactants and products (and any catalysts, if applicable) are present in the same phase. By this definition, homogeneous equilibria take place in solutions. These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:

$$C_2H_2(aq) + 2Br_2(aq) \rightleftharpoons C_2H_2Br_2(aq) \qquad K_C = \frac{[C_2H_2Br_2]}{[C_2H_2][Br_2]^2}$$

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad K_C = \frac{[I_3^-]}{[I_2][I^-]}$$

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \qquad K_C = \frac{[H_3O^+][F^-}{[HF]}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_C = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products. A relation between these two K values may be simply derived from the ideal gas equation and the definition of molarity:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$= MRT$$

Where P is partial pressure, V is volume, n is molar amount, R is the gas constant, T is temperature, and M is molar concentration.

For the gas-phase reaction

$$mA + nB \rightleftharpoons xC + yD:$$

$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n}$$

$$= \frac{([C]xRT)^x ([D]xRT)^y}{([A]xRT)^m ([BxRT)^n}$$

$$= \frac{[C]^x [D]^x}{[A]^m [B]^n} x \frac{(RT)^{x+y}}{(RT)^{m+n}}$$

$$= K_C (RT)^{(x+y)-(m+n)}$$

$$= K_C (RT)^{\Delta n}$$

And so, the relationship between K_C and K_P is

$$K_P = K_C(RT)^{\Delta n}$$

Where Δn is the difference in the molar amounts of product and reactant gases, in this case:

$$\Delta n = (x + y) - (m + n)$$

Example 7.3: Calculation of *KP*

Write the equations relating ***Kc*** to ***KP*** for each of the following reactions:

a. $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

b. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

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

d. K_c is equal to 0.28 for the following reaction at 900 °C:

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$$

What is K_P at this temperature?

Solution

a. $\Delta n = (2) - (1) = 1$

$KP = Kc\,(RT)^{\Delta n} = Kc\,(RT)^{1} = Kc\,(RT)$

b. $(b)\ \Delta n = (2) - (2) = 0$

$KP = Kc\,(RT)^{\Delta n} = Kc\,(RT)^{0} = Kc$

c. $(c)\ \Delta n = (2) - (1 + 3) = -2$

$KP = Kc(RT)^{\Delta n} = Kc\,(RT)^{-2} = \frac{Kc}{(RT)^2}$

D' $K_P = K_C(RT)^{\Delta n} = \frac{0.28}{[(0.0821)(1173)]^2} = 3.0X10^{-5}$

Heterogeneous Equilibria

A heterogeneous equilibrium involves reactants and products in two or more different phases, as illustrated by the following examples:

Cont'd

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K_C = [Pb^{2+}][Cl^-]^2$$

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad K_C = \frac{1}{[CO_2]}$$

$$C(s) + 2S(g) \rightleftharpoons CS_2(g) \qquad K_C = \frac{[CS_2]}{[S]^2}$$

$$br_2(l) \rightleftharpoons Br_2(g) \qquad K_C = [Br_2]$$

Le Chatelier's principle

A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates. If an equilibrium system is **stressed**, the system will experience a shift in response to the stress that re-establishes equilibrium.

Reaction rates are affected primarily by concentrations, as described by the reaction's rate law, and temperature, as described by the Arrhenius equation. Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

If the system is stressed by adding reactant, either H_2 or I_2, the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

$$\mathbf{rate}_f > \mathbf{rate}_r$$

Raising the temperature of the system is causing to increasing the amount of a product, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

According to Le Chatelier's principle, if the pressure at equilibrium is increased then the reaction will proceed in that direction where the pressure is reduced. Since the pressure depends upon the number of moles, on increasing the pressure the reaction will proceed in that direction where the number of moles are reduced. If the pressure at equilibrium is decreased then the reaction will proceed in that direction where the number of moles is more.

Equilibrium calculation

Iodine molecules react reversibly with iodine ions to produce triiodide ions.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3}M before reaction gives an equilibrium concentration of 6.61×10^{-4}M, what is the equilibrium constant for the reaction?

Solution

To calculate the equilibrium constants, constant are needed for all the reactant and products:

$$\boldsymbol{K_c = \frac{[I^{3-}]}{[I_2][I^-]}}$$

Provided are the initial concentrations of the reactants and the equilibrium concentration of the product. Use this information to derive terms for the equilibrium concentrations of reactants, presenting all the information in the reaction table.

	$I_2(aq)$ +	$I^-(aq)$ ⇌	$I_3^-(aq)$
Initial concentration (M)	1.000×10^{-3}	1.000×10^{-3}	0
Change (M)	-x	-x	+x
Equilibrium conc.(M)	1.000×10^{-3}-x	1.000×10^{-3}-x	X

At equilibrium the concentration of I_2 is 6.61×10^{-4}M so that

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$

$$X = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$

$$= 3.39 \times 10^{-4} M$$

The table may now be update with numerical values for all its concentrations:

	$I_2(aq)$	+ $I^-(aq)$	⇌ $I_3^-(aq)$
Initial concentration (M)	1.000×10^{-3}	1.000×10^{-3}	0
Change (M)	-3.39×10^{-4}	-3.39×10^{-4}	$+3.39 \times 10^{-4}$
Equilibrium conc.(M)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

Finally, substitute the equilibrium concentrations into the K expression and solve:

$$K_c = \frac{[I^{3-}]}{[I_2][I^-]}$$

$$= \frac{3.39x10^{-4}M}{(6.61x10^{-4}M)(6.61x10^{-4}M)} = 776$$

Relative Strength of Acids and Bases

- The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak.

Strong acids	Strong bases
$HClO_4$ perchloric acid	LiOH lithium hydroxide
HCl hydrochloric acid	NaOH sodium hydroxide
HBr hydrobromic acid	KOH potassium hydroxide
HI hydroiodic acid	$Ca(OH)_2$ calcium hydroxide
HNO_3 nitric acid	Sr(OH)2 strontium hydroxide
H_2SO_4 sulfuric acid	Ba(OH)2 barium hydroxide

The equilibrium constant for an acid is called the acid-ionization constant, *K*a. For the reaction of an acid HA:

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$, the ionization constant is written

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Just as for acids, the relative strength of a base is reflected in the magnitude of its base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

The ionization constant is written as

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

Example 7.4

Calculating ionization constants for conjugate acid-base pairs

Use the K_b for the nitrite ion, to calculate the K_a for its conjugate acid.

Solution

K_a for NO_2^- is given in this section as 2.17×10^{11}. The conjugate acid of NO_2^- is HNO_2; HNO_2 can be calculated using the relationship:

$$K_A x K_b = 1.0 x 10^{-14} = K_w$$

Solving for $K_a = \frac{K_w}{K_b} = \frac{1.0 x 10^{-14}}{2.17 x 10^{-11}} = 4.6 x 10^{-4}$

Buffers Solution

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added Figure 7.12. A solution of acetic acid and sodium acetate ($CH_3COOH + CH_3COONa$) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($NH_3(aq) + NH_4Cl(aq)$).

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

H_3O^+ added, equilibrium position shifts to the left

$$CH_3COOH(aq) \leftarrow CH_3COO^-(aq) + H_3O^+$$

OH^- added, equilibrium position shifts to the right

$$OH^- + CH_3COOH(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

Cont'd

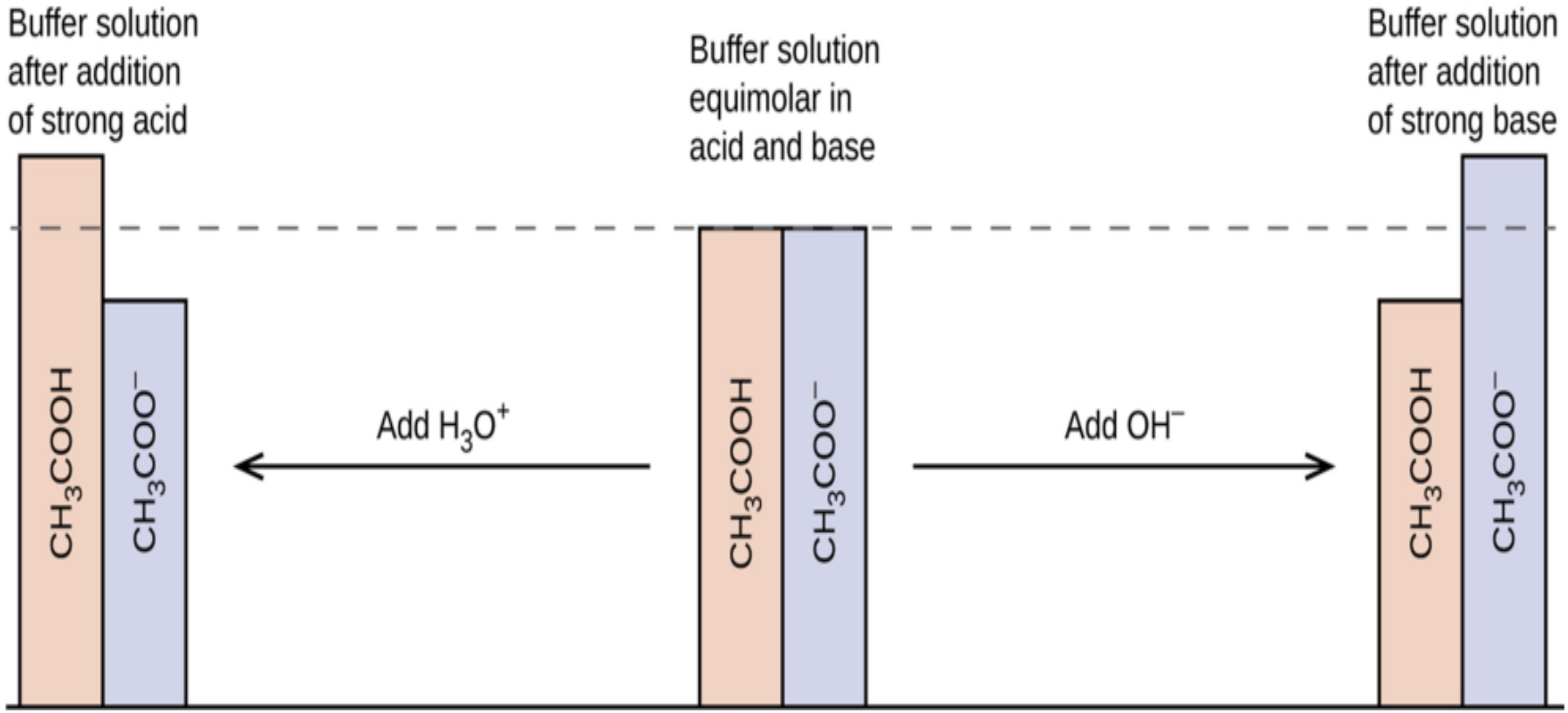


Figure 7.1: Buffering action in a mixture of acetic acid and acetate salt.

pH of a Buffer Solution:

(b) pH of buffer solution: (pH ≈ pK_a of HA)

$$HA_{(aq)} \rightleftharpoons H^+ + A^-_{(aq)}$$

	$HA_{(aq)}$	H^+	$A^-_{(aq)}$
Initial	"M"	0	"A"
Change	–x	+x	+x
Equil	M – x	x	A + x

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x(A+x)}{(M-x)}$$

Since K_a is usually small ($< \sim 10^{-4}$):

$M - x \approx M$ and $A + x \approx A$

thus, $K_a \approx x(A)/M$ or simply,

$$[H^+] \approx \frac{K_a[HA]}{[A^-]}$$ **(general buffer system)**

and $$[H^+] \approx K_a \left(\frac{\text{moles HA}}{\text{moles } A^-}\right)$$

- **Henderson-Hasselbach Eqn:**

$$[H^+] \approx \frac{K_a[HA]}{[A^-]} \qquad \text{(general buffer system)}$$

Again assuming that x is small, you can take the log of both sides and rearrange to get the Henderson-Hasselbach equation;

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

The HH equation is optional; if x is small approximation does not work, you need to use the more general method anyway...

The acid ionization constant is:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

By rearranging, you get an equation for the H_3O^+ concentration.

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

- Taking the negative logarithm of both sides of the equation we obtain:

$$-\log[H_3O^+] = -\log(K_a) - \log\frac{[HA]}{[A^-]}$$

- The previous equation can be rewritten

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

- More generally, you can write

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

- This equation relates the pH of a buffer to the concentrations of the conjugate acid and base.

Example: Calculate the pH of ammonium hydroxide – ammonium chloride buffer solution that is 0.1 M in ammonium hydroxide and 0.01 M in ammonium chloride. (pKb of NH_4OH = 9.25).

Solution: Here, [Base] = 0.1 M and [Salt} = 0.01 M

Since $\mathbf{p}K_b = 9.25$;

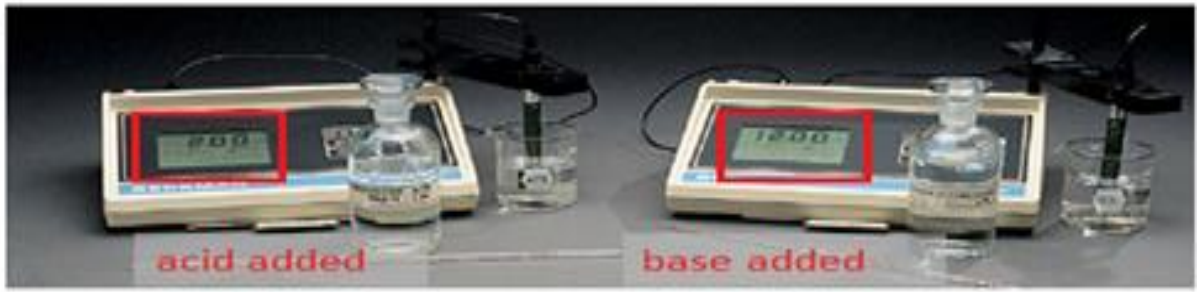
According to Henderson equation, $pOH = pK_b + \log \frac{[Salt]}{[Base]}$

Substituting the values in Handerson eqation, we get

$$pOH = 9.25 + \log (0.01 / 0.1) = 9.25 + \log 0.1 = 9.25 - 1.0 = 8.25$$

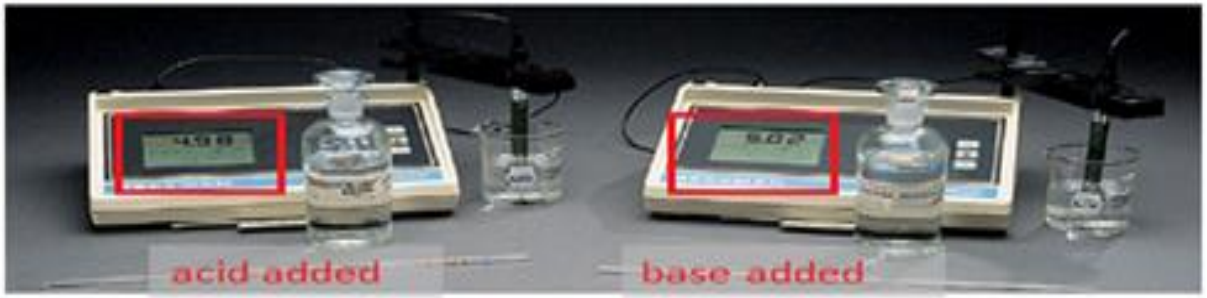
The effect of addition of acid or base to ...





an unbuffered solution





or a buffered solution

Calculating the Effect of Added H_3O^+ or OH^- on Buffer pH

PROBLEM: Calculate the pH:

(a) of a buffer solution consisting of 0.50M CH_3COOH and 0.50M CH_3COONa

(b) after adding 0.020mol of solid NaOH to 1.0L of the buffer solution in part (a)

(c) after adding 0.020mol of HCl to 1.0L of the buffer solution in part (a)

K_a of $CH_3COOH = 1.8 \times 10^{-5}$. (Assume the additions cause negligible volume changes.

PLAN: We know K_a and can find initial concentrations of conjugate acid and base. Make assumptions about the amount of acid dissociating relative to its initial concentration. Proceed step-wise through changes in the system.

SOLUTION: **(a)**

Concentration (M)	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$			
Initial	0.50	-	0.50	0
Change	$-x$	-	$+x$	$+x$
Equilibrium	$0.50-x$	-	$0.50+x$	x

$[H_3O^+] = x$ $[CH_3COOH]_{equil} \approx 0.50M$ $[CH_3COO^-]_{initial} \approx 0.50M$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \qquad [H_3O^+] = x = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} = 1.8\times10^{-5}M$$

Check the assumption: $1.8\times10^{-5}/0.50 \times 100 = 3.6\times10^{-3}$ %

(b)

$$[OH^-]_{added} = \frac{0.020 \text{ mol}}{1.0\text{L soln}} = 0.020M \text{ NaOH}$$

Concentration (M)	**$CH_3COOH(aq)$**	**+ $OH^-(aq)$**	**⇌ $CH_3COO^-(aq)$**	**+ $H_2O(l)$**
Before addition	0.50	-	0.50	-
Addition	-	0.020	-	-
After addition	0.48	0	0.52	-

Set up a ***reaction table*** with the new values.

Concentration (M)	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$			
Initial	0.48	-	0.52	0
Change	$-x$	-	$+x$	$+x$
Equilibrium	$0.48 - x$	-	$0.52 + x$	x

$$[H_3O^+] = 1.8\times10^{-5}\ \frac{0.48}{0.52} = 1.7\times10^{-5}$$

pH = 4.77

(c) $$[H_3O^+]_{added} = \frac{0.020\ \text{mol}}{1.0\text{L soln}} = 0.020\text{M } H_3O^+$$

Before addition	0.50	-	0.50	-
Addition	-	0.020	-	-
After addition	0.48	0	0.52	-

Set up a ***reaction table*** with the new values.

Concentration (M)	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$		
Initial	0.52	0.48	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.52 - x$	$0.48 + x$	x

$$[H_3O^+] = 1.8 \times 10^{-5} \frac{0.52}{0.48} = 2.0 \times 10^{-5}$$

pH = 4.70