Chemical Equilibrium

Fast Initial Step

$$Step\ 1:\ \ NO + Br_2 \rightleftharpoons NOBr_2$$

- Because Rate$_f$ = Rate$_r$,

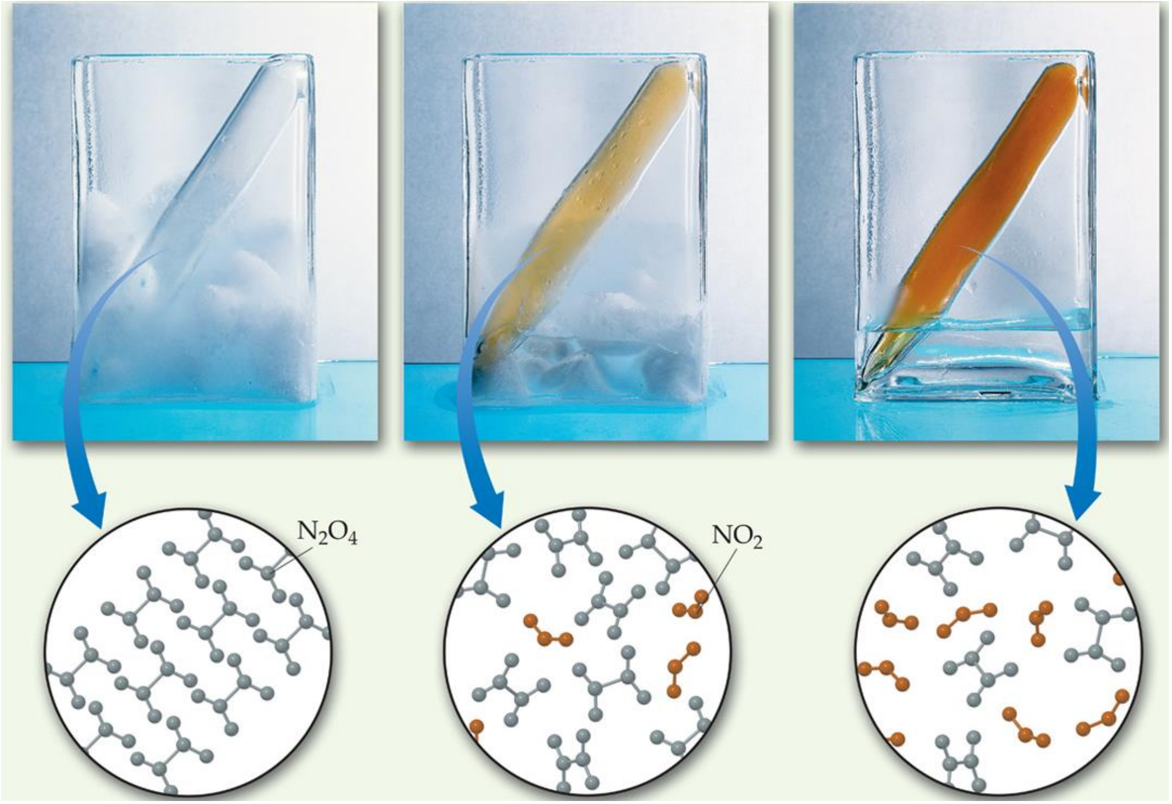
$$k_1\,[NO]\,[Br_2] = k_{-1}\,[NOBr_2]$$

Solving for [NOBr$_2$] gives us

$$\frac{k_1}{k_{-1}}\,[NO]\,[Br_2] = [NOBr_2]$$

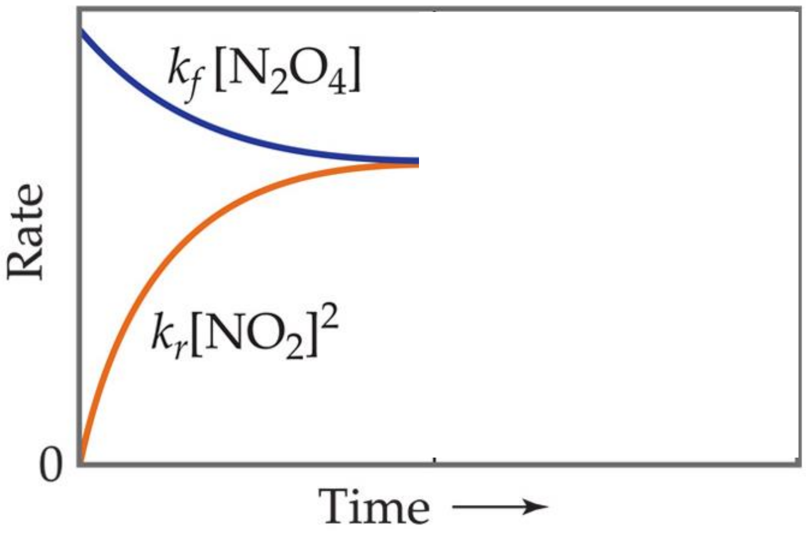
Can also write as: $$\frac{k_1}{k_{-1}} = \frac{[NOBr_2]}{[NO]\,[Br_2]}$$

The Concept of Equilibrium



Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.

The Concept of Equilibrium

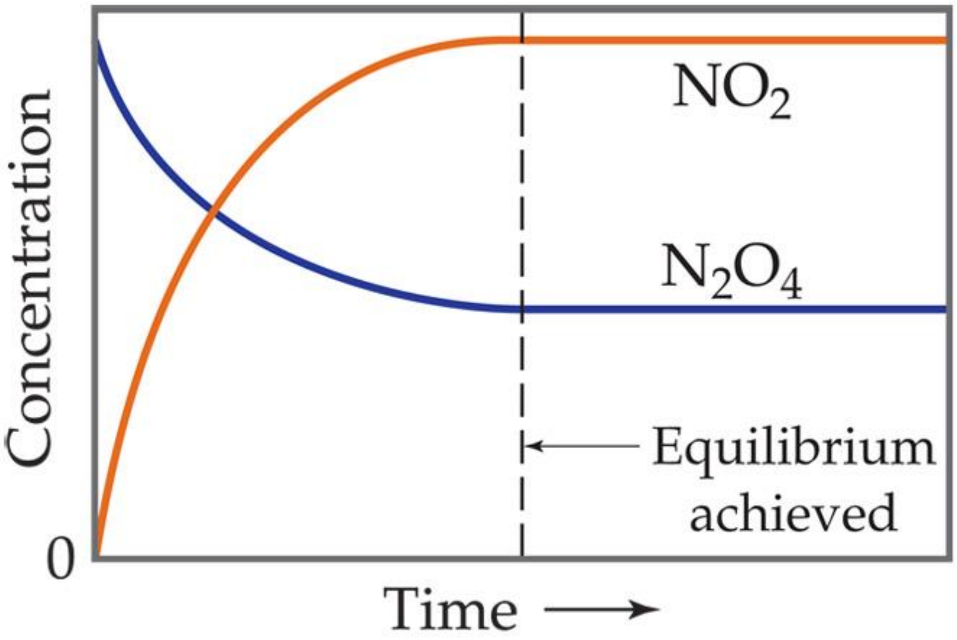


$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

- As a system approaches equilibrium, both the forward and reverse reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding at the same rate.

A System at Equilibrium

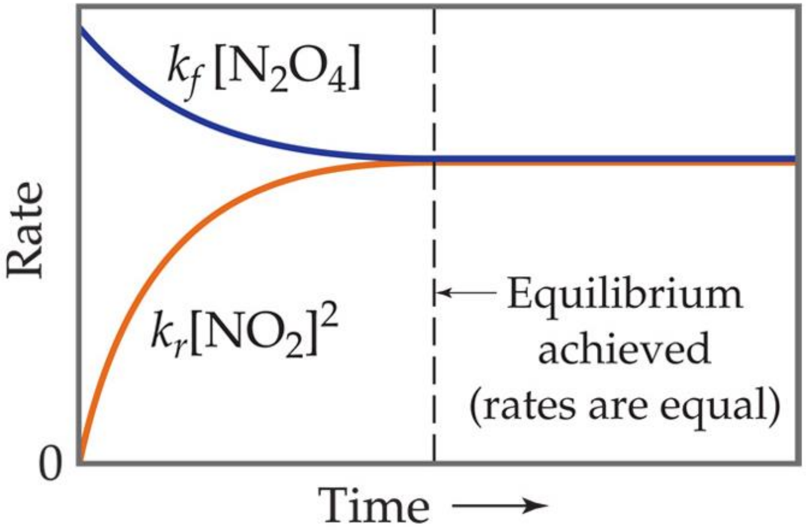
Once equilibrium is achieved, the *amount* of each reactant and product remains constant.



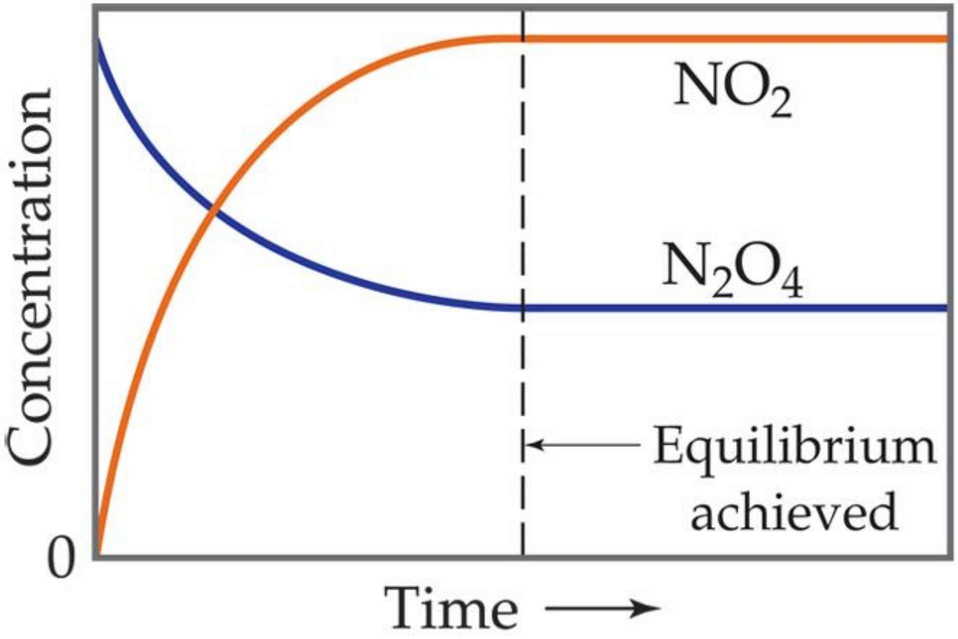
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

A System at Equilibrium

Rates become equal



Concentrations become constant



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

Depicting Equilibrium

In a system at equilibrium, both the forward and reverse reactions are running simultaneously. We write the chemical equation with a double arrow:

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

The Equilibrium Constant

The Equilibrium Constant

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

Forward reaction:

Reverse reaction:

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

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

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

Rate law

$$rate = k_f\,[N_2O_4]$$

Rate Law

$$rate = k_r\,[NO_2]^2$$

The Equilibrium Constant

At equilibrium

$$rate_f = rate_b$$

$$k_f\left[N_2O_4\right] = k_r\left[NO_2\right]^2$$

Rearranging gives:

$$\frac{k_f}{k_r} = \frac{\left[NO_2\right]^2}{\left[N_2O_4\right]}$$

The Equilibrium Constant

The ratio of the rate constants is a constant (as long as T is constant).

The expression becomes

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

The Equilibrium Constant

To generalize, the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

Has the equilibrium expression:

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

This expression is true even if you don’t know the elementary reaction mechanism.

SAMPLE EXERCISE 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:

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

(b) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

(c) $Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

(a) $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$,

(b) $Cd^{2+}(aq) + 4\,Br^-(aq) \rightleftharpoons CdBr_4{}^{2-}(aq)$.

SAMPLE EXERCISE 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:

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(b) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$
(c) $Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

Solution

Analyze: We are given three equations and are asked to write an equilibrium-constant expression for each.

Plan: Using the law of mass action, we write each expression as a quotient having the product concentration terms in the numerator and the reactant concentration terms in the denominator. Each term is raised to the power of its coefficient in the balanced chemical equation.

Solve:

$$\textbf{(a)}\ K_c = \frac{[O_2]^3}{[O_3]^2},\ \textbf{(b)}\ K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]},\ \textbf{(c)}\ K_c = \frac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$$

PRACTICE EXERCISE

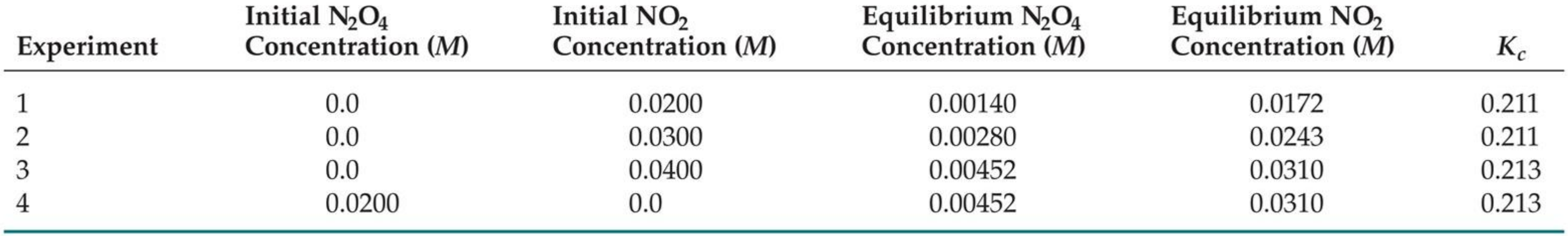
Write the equilibrium-constant expression, K_c for

(a) $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$,
(b) $Cd^{2+}(aq) + 4\,Br^-(aq) \rightleftharpoons CdBr_4{}^{2-}(aq)$.

Answers: $$\textbf{(a)}\ K_c = \frac{[HI]^2}{[H_2][I_2]};\ \textbf{(b)}\ K_c = \frac{[CdBr_4{}^{2-}]}{[Cd^{2+}][Br^-]^4}$$

Equilibrium Can Be Reached from Either Direction

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

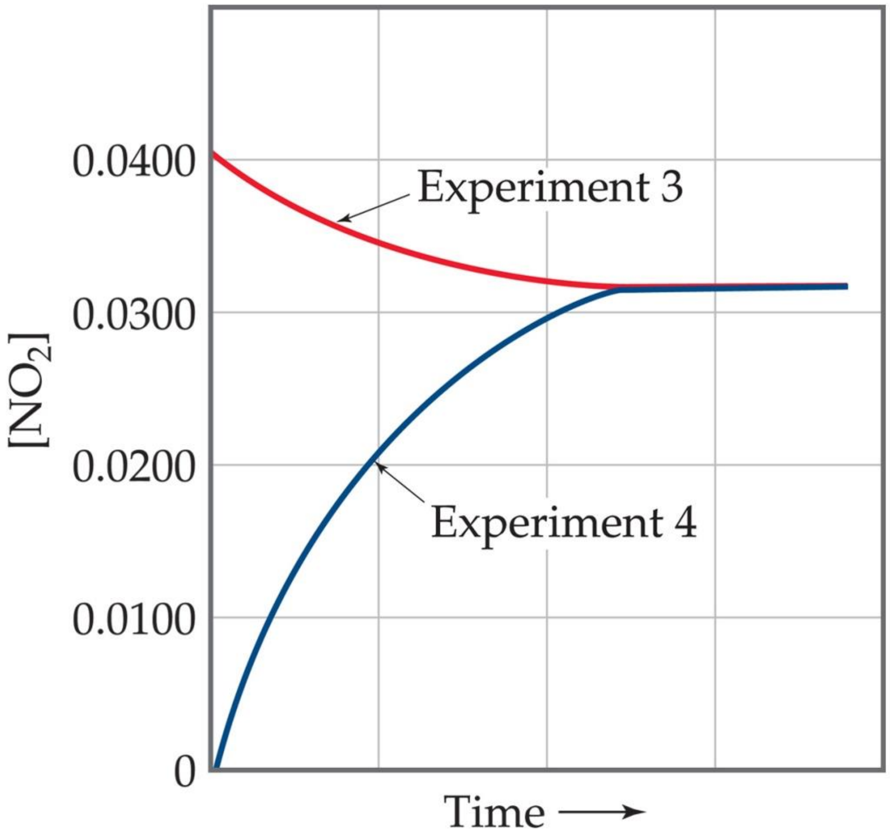


Experiment	Initial N_2O_4 Concentration (M)	Initial NO_2 Concentration (M)	Equilibrium N_2O_4 Concentration (M)	Equilibrium NO_2 Concentration (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

K_c, the final ratio of $[NO_2]^2$ to $[N_2O_4]$, reaches a constant no matter what the initial concentrations of NO_2 and N_2O_4 are (with const T).

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

Equilibrium Can Be Reached from Either Direction

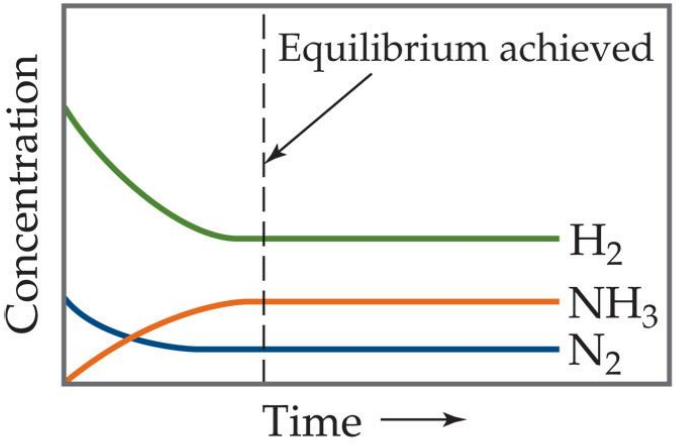


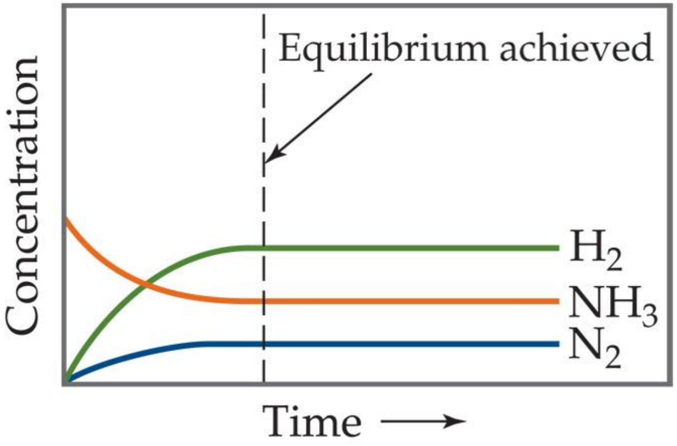
This graph shows data from the last two trials from the table.

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

Equilibrium Can Be Reached from Either Direction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

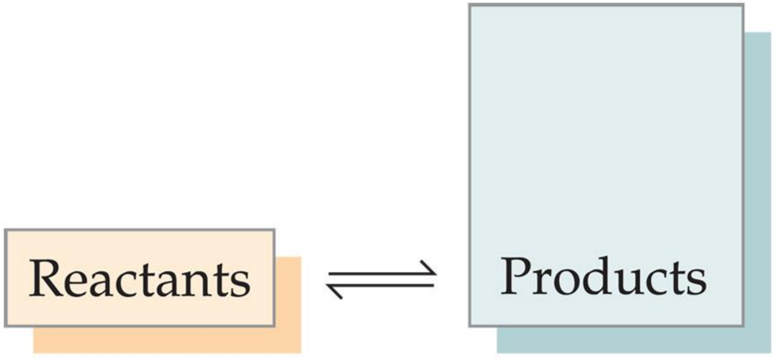




It does not matter whether we start with N_2 and H_2 or whether we start with NH_3. We will have the same proportions of all three substances at equilibrium.

What is the equilibrium expression?

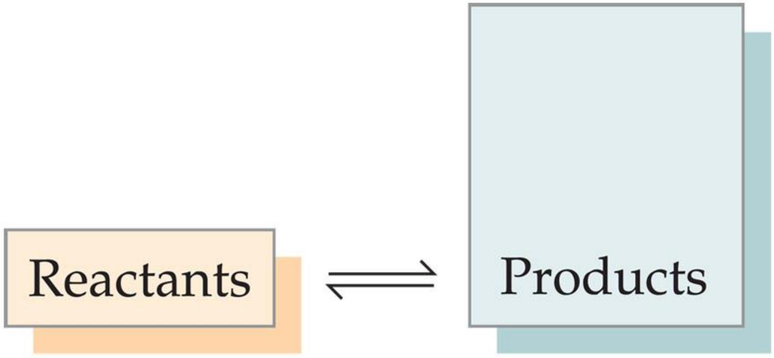
What Does the Value of *K* Mean?



(a) $K >> 1$

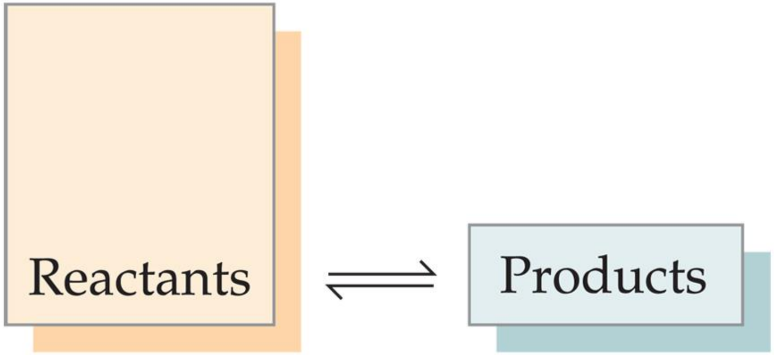
- If $K >> 1$, the reaction is *product-favored*; product predominates at equilibrium.

What Does the Value of *K* Mean?



(a) $K >> 1$

- If *K* >> 1, the reaction is *product-favored*; product predominates at equilibrium.



(b) $K << 1$

- If K << 1, the reaction is *reactant-favored*; reactant predominates at equilibrium.

Manipulating Equilibrium Constants

The equilibrium constant of a reaction in the reverse reaction is the reciprocal of the equilibrium constant of the forward reaction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$$

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K'_{eq} = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{0.212}$$

$$= 4.72$$

Manipulating Equilibrium Constants

The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power that is equal to that number.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$$

$$2N_2O_4(g) \rightleftharpoons 4NO_2(g) \qquad K'_{eq} = \frac{[NO_2]^4}{[N_2O_4]^2} = (0.212)^2$$

Manipulating Equilibrium Constants

The equilibrium constant for a net reaction made up of two or more steps can be found from the equilibrium constants for the individual steps.`

At 1565 K we have these equilibrium constants:

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g) \qquad K_1 = 1.6 \times 10^{-11}$$

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g) \qquad K_2 = 1.3 \times 10^{-10}$$

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \qquad K_3 = ?$$

ans=2.9

The Equilibrium Constant

Because pressure is proportional to concentration for gases, the equilibrium expression can also be written in terms of partial pressures (instead of concentration):

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Mixed versions are also used sometimes:

$$K_{mixed} = \frac{(P_C)^c \, [D]^d}{[A]^a \, (P_B)^b}$$

Relationship between K_c and K_p

- From the ideal gas law we know that

$$PV = nRT$$

$$P = \frac{n}{V}RT$$ = Pressure in terms of concentration

$$P_A = \frac{n_A}{V}RT = [A]\,RT$$

Relationship between K_c and K_p

Substituting P=[A]RT into the expression for K_p for each substance, the relationship between K_c and K_p becomes

$$K_p = K_c\,(RT)^{\Delta n}$$

Where:

Δn = (moles of gaseous product) – (moles of gaseous reactant)

Hint: ‘products–reactants’ and ‘products over reactants’ is a common theme in chemistry.

Heterogeneous Equilibrium

The Concentrations of Solids and Liquids Are Essentially Constant

Concentrations of liquids and solids can be obtained by dividing the density of the substance by its molar mass—and both of these are constants at constant temperature.

$$\frac{density}{molar\ mass} = \frac{g/L}{g/mol} = \frac{mol}{L}$$

The Concentrations of Solids and Liquids Are Essentially Constant

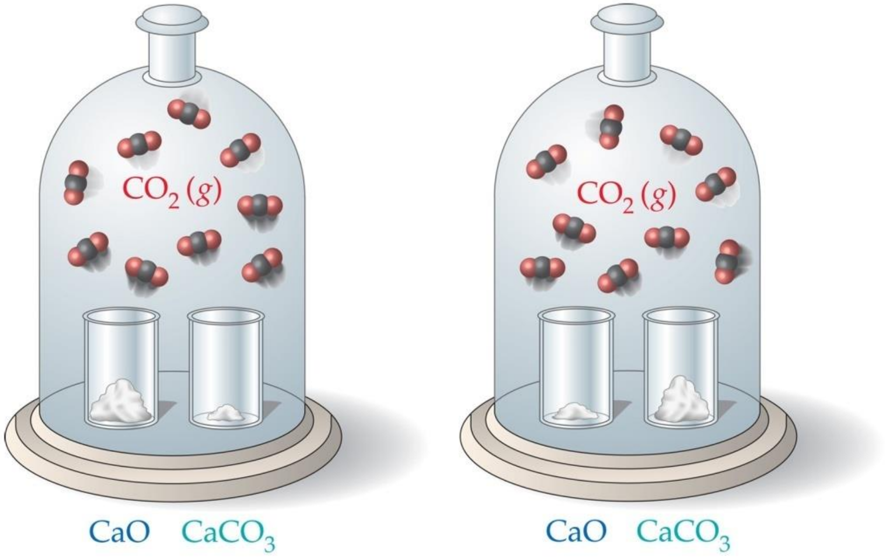
Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression

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

$$K_c = [Pb^{2+}]\,[Cl^{-}]^2$$

$$CaCO_{3\,(s)} \rightleftharpoons CO_{2\,(g)} + CaO_{(s)}$$

As long as some $CaCO_3$ or CaO remain in the system, the amount of CO_2 above the solid will remain the same.



What Are the Equilibrium Expressions for These Equilibria?

$$SnO_2(s) + 2CO(g) \rightleftharpoons Sn(s) + 2CO_2(g)$$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$$

The real scoop: units of equilibrium constants

Equilibrium constants are *really* defined in terms of **activity**, not concentration.

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

becomes:

$$K_c = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

Activity is unitless, so K is unitless.

$$for\ pure\ liquids:\ a = 1.0$$

$$for\ pure\ solids:\ a = 1.0$$

$$for\ solutions:\ a_A = [A]\,\gamma$$

$$for\ dilute\ solutions:\ \gamma = 1.0\ M^{-1}$$

Equilibrium Calculations

Equilibrium Calculations

A closed system initially containing
1.000×10^{-3} M H_2 and 2.000×10^{-3} M I_2
At 448°C is allowed to reach equilibrium.
Analysis of the equilibrium mixture shows
that the concentration of HI is 1.87×10^{-3} M.
Calculate K_c at 448°C for the reaction:

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

What Do We Know?

ICE method:

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
At Equilibrium			1.87×10^{-3}

[HI] Increases by 1.87×10^{-3} *M*

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

Stoichiometry tells us $[H_2]$ and $[I_2]$ decrease by half as much

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

We can now calculate the equilibrium concentrations of all three compounds…

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
At equilibrium	6.5×10^{-5}	1.065×10^{-3}	1.87×10^{-3}

…and, therefore, the equilibrium constant

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

$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})}$$

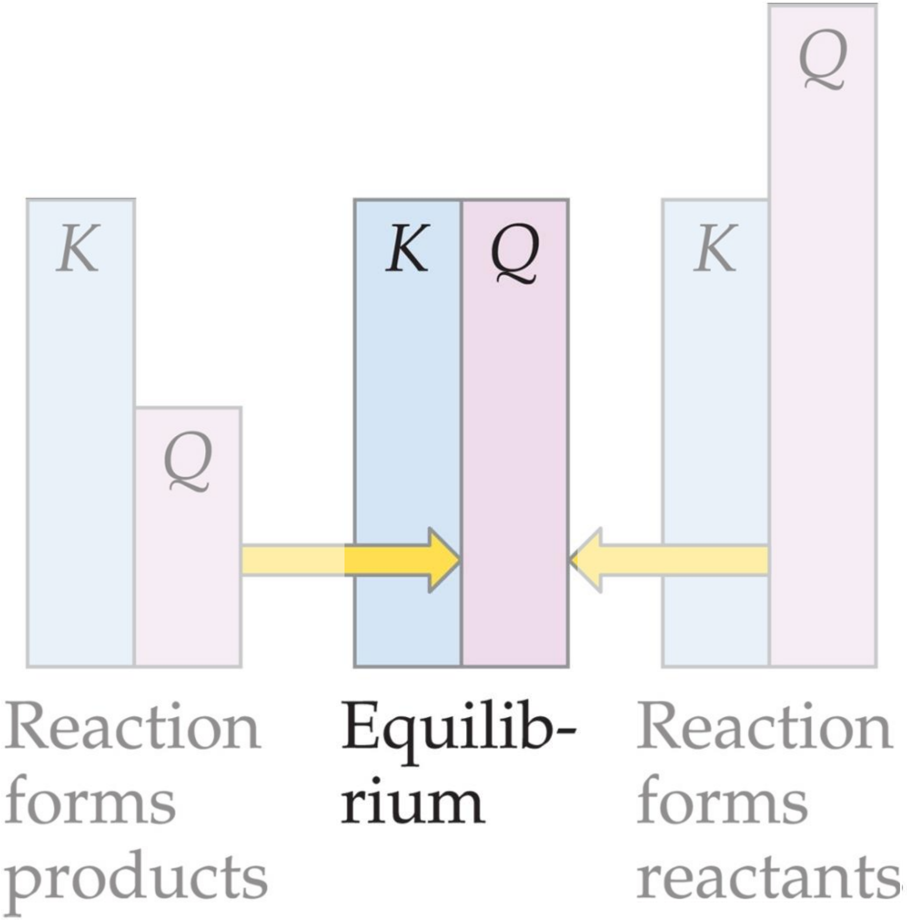
$$= 51$$

The Reaction Quotient (*Q*)

- To calculate *Q*, one substitutes the initial concentrations on reactants and products into the equilibrium expression.
- *Q* gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.

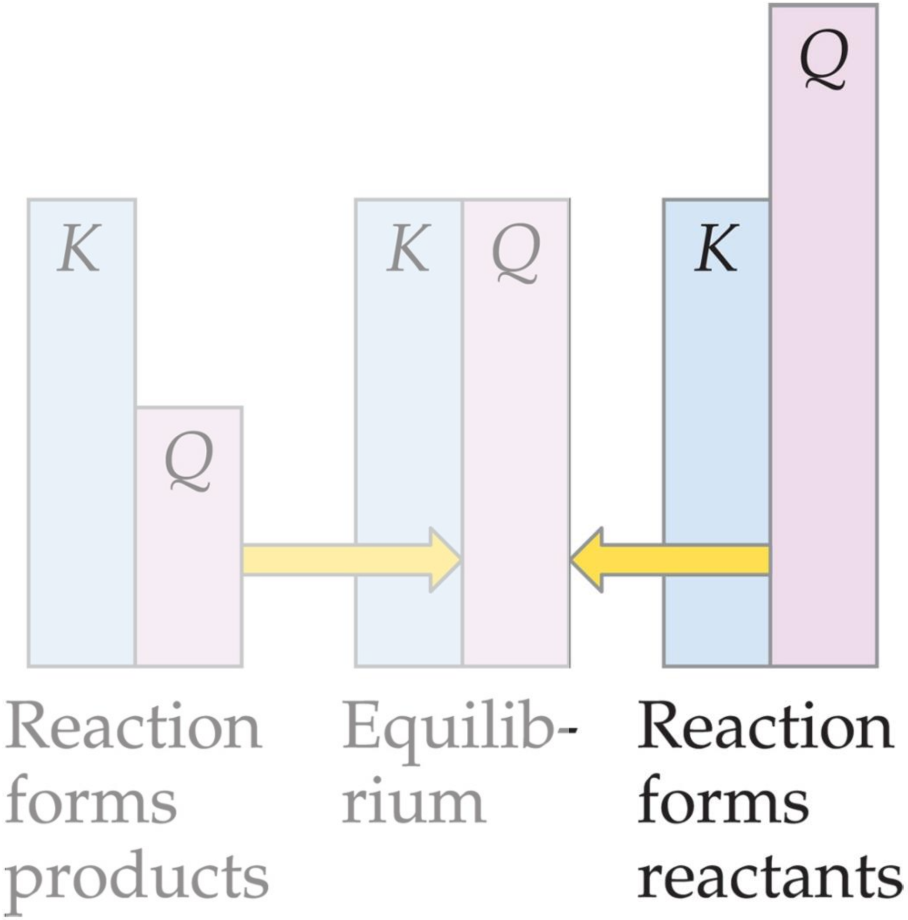
If $Q = K$,

the system is at equilibrium.



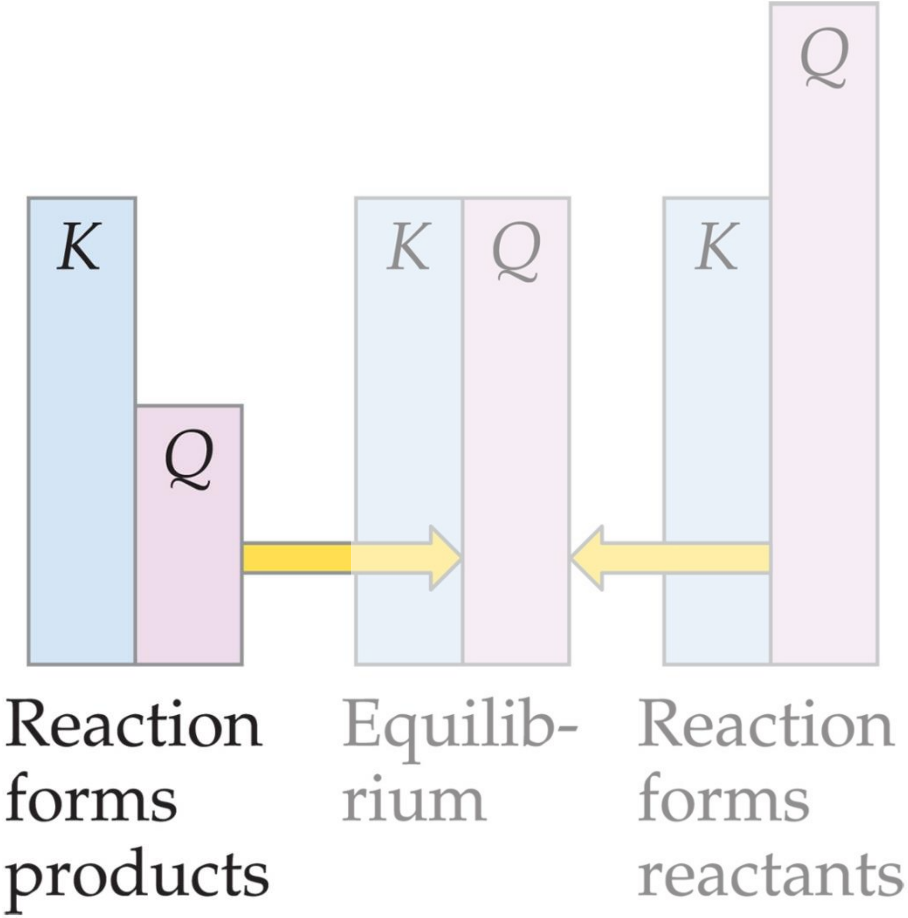
If $Q > K$,

there is too much product and the equilibrium shifts to the left.



If $Q < K$,

there is too much reactant, and the equilibrium shifts to the right.



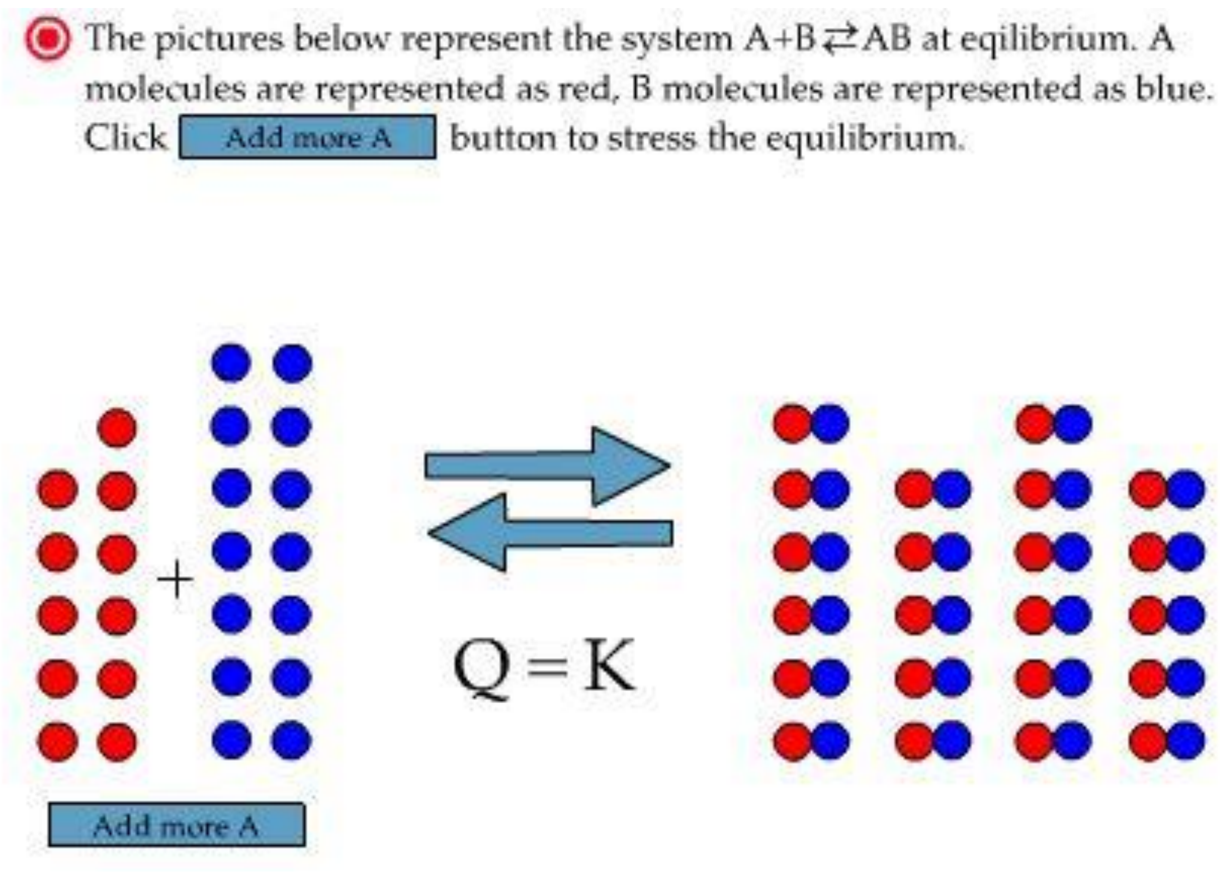
Le Châtelier’s Principle

Le Châtelier’s Principle

“If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.”

Systems shift from “Q” towards “K”.

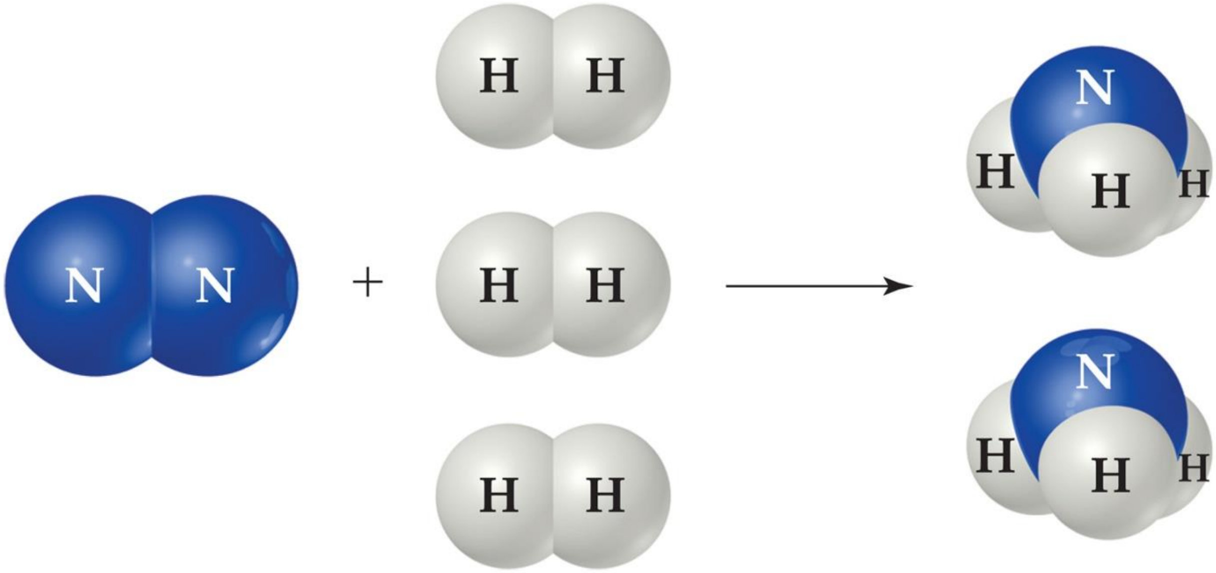
What Happens When More of a Reactant Is Added to a System?



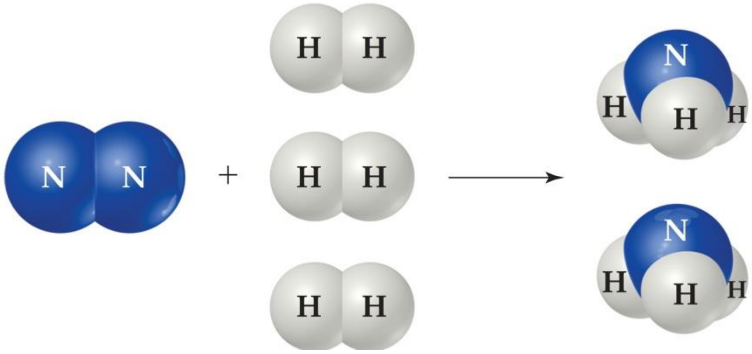
● The pictures below represent the system $A+B \rightleftarrows AB$ at eqilibrium. A molecules are represented as red, B molecules are represented as blue. Click Add more A button to stress the equilibrium.

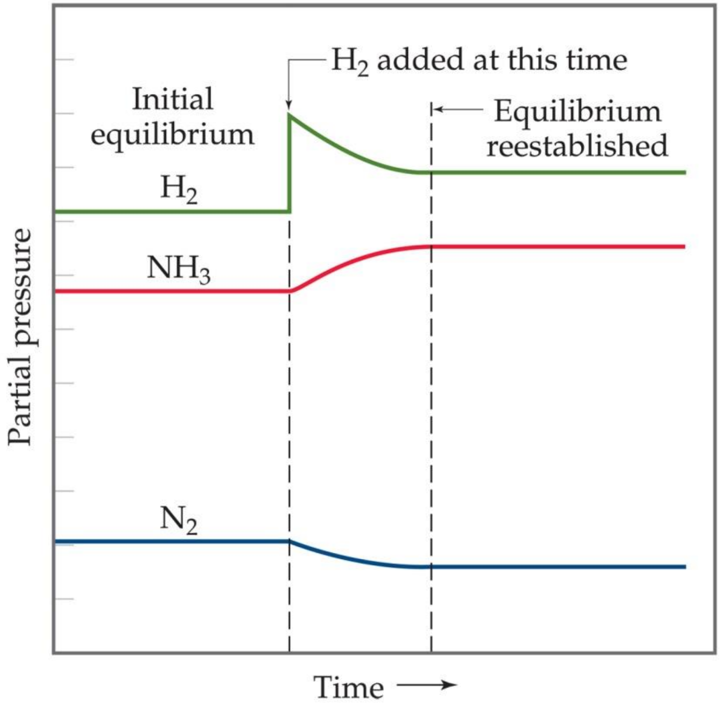
The Haber Process

The transformation of nitrogen and hydrogen into ammonia (NH_3) is of tremendous significance in agriculture, where ammonia-based fertilizers are of utmost importance.



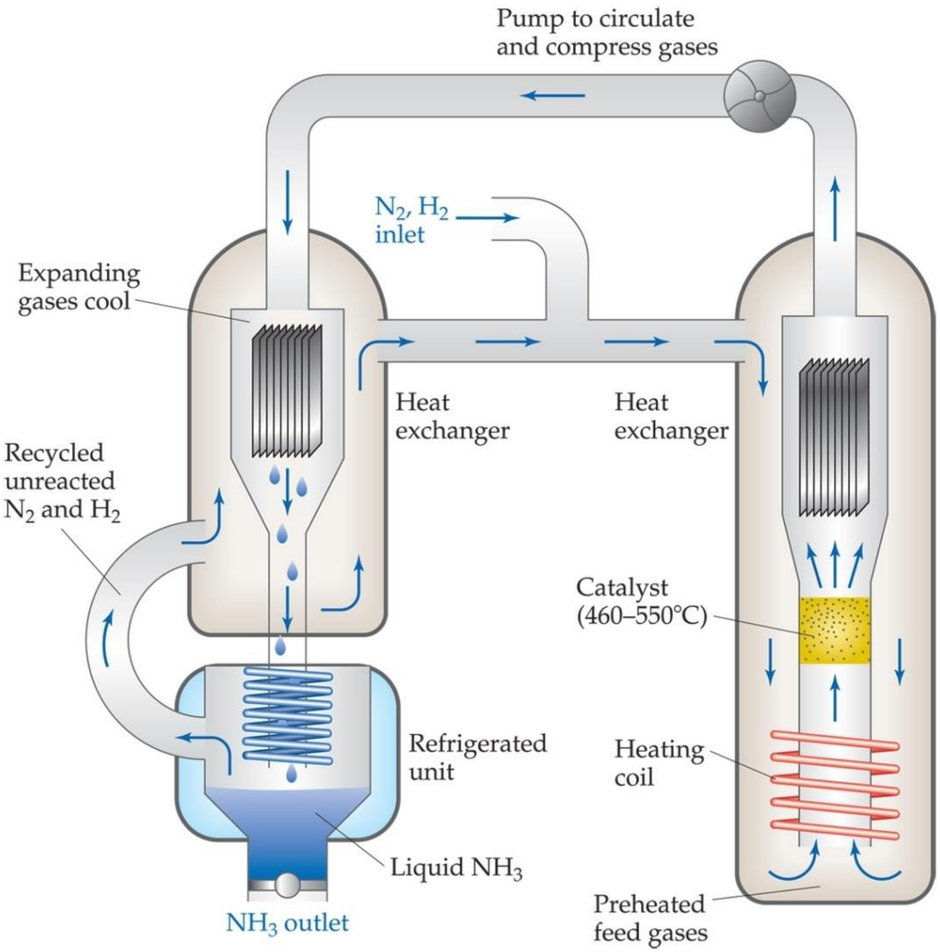
The Haber Process





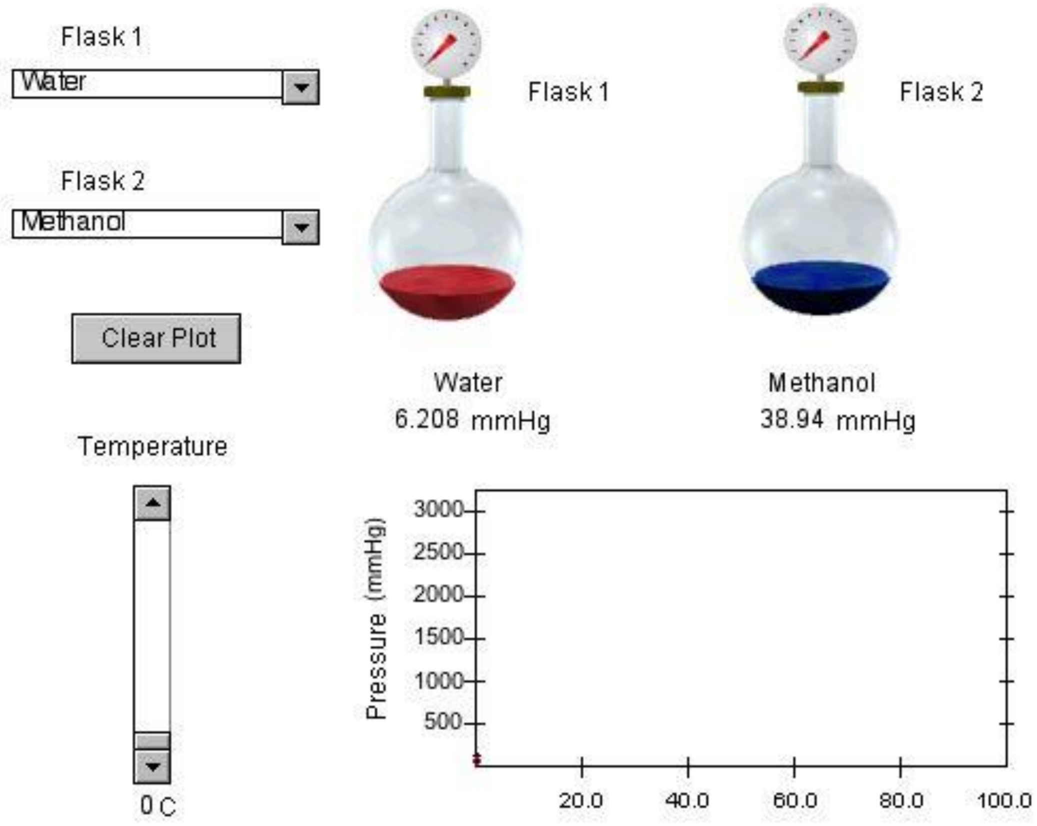
If H_2 is added to the system, N_2 will be consumed and the two reagents will form more NH_3.

The Haber Process



This apparatus helps push the equilibrium to the right by removing the ammonia (NH_3) from the system as a liquid.

The Effect of Changes in Pressure



Flask 1: Water

Flask 2: Methanol

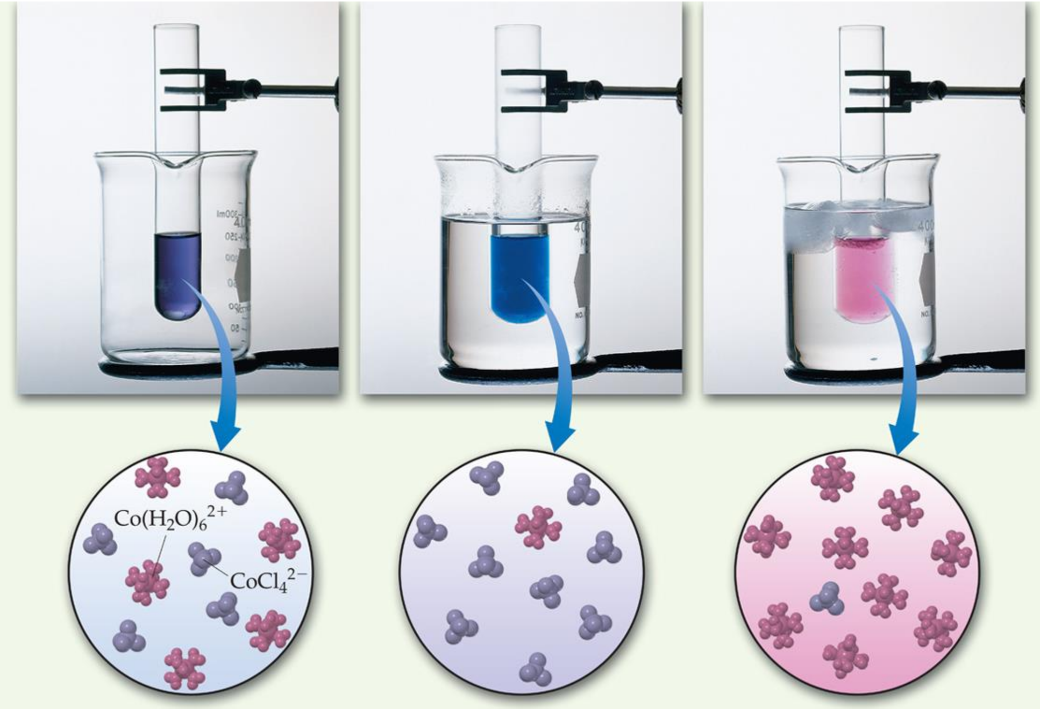
Water 6.208 mmHg

Methanol 38.94 mmHg

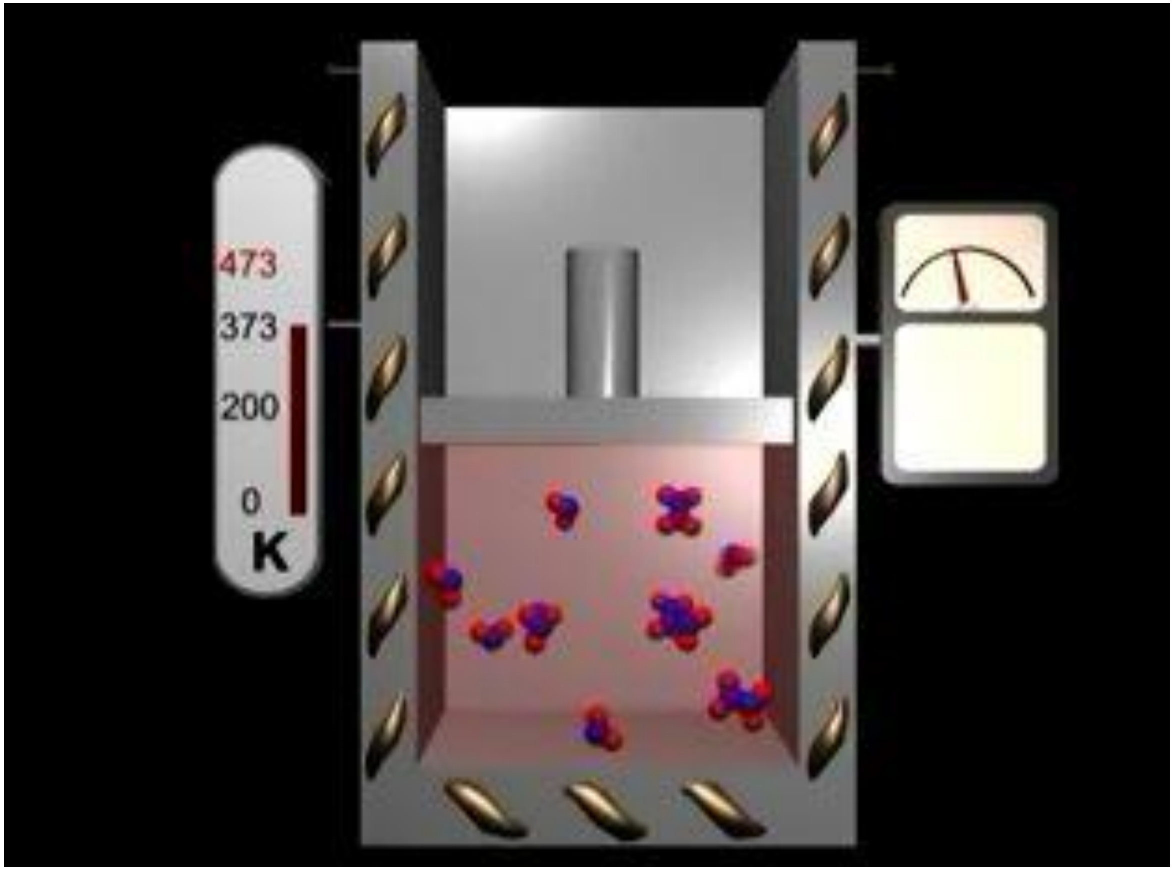
Temperature 0 C

The Effect of Changes in Temperature

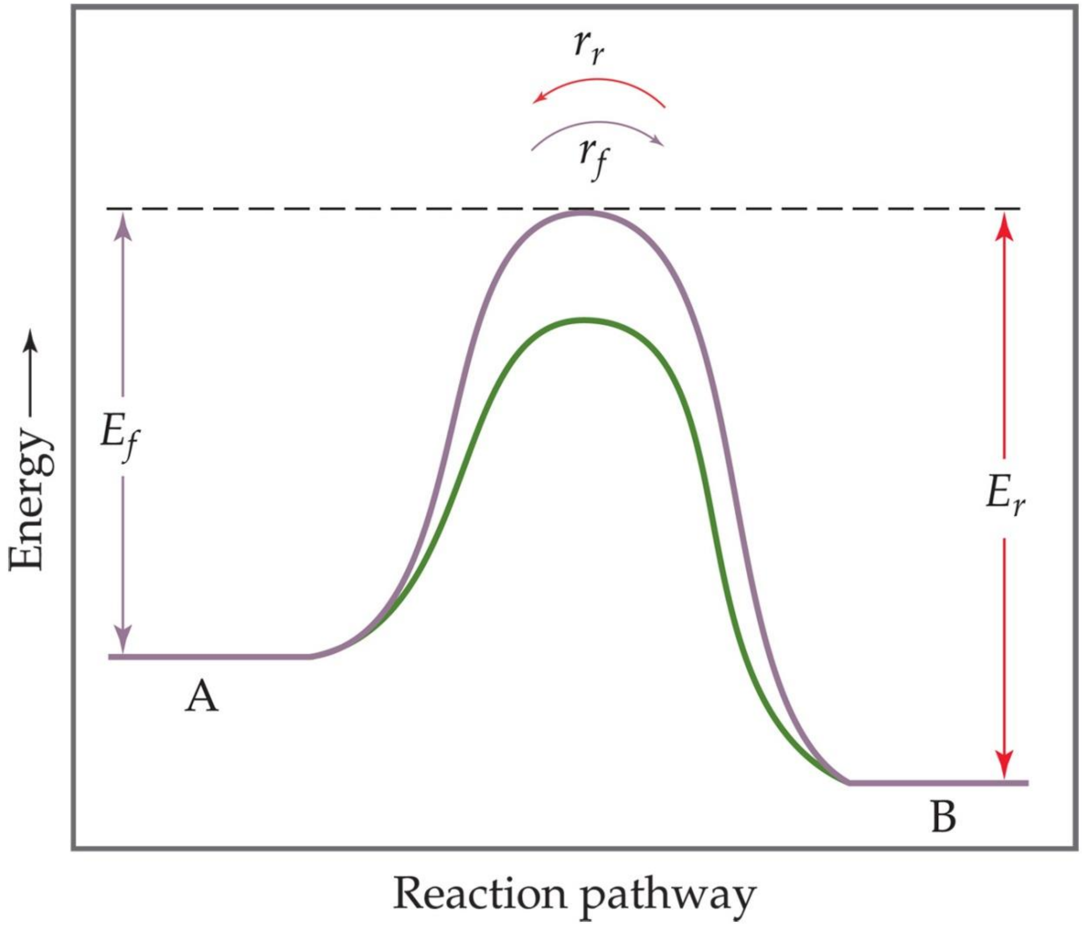
$$Co(H_2O)_6^{2+}{}_{(aq)} + 4\ Cl_{(aq)} \rightleftharpoons CoCl_{4\ (aq)} + 6\ H_2O_{\ (l)}$$



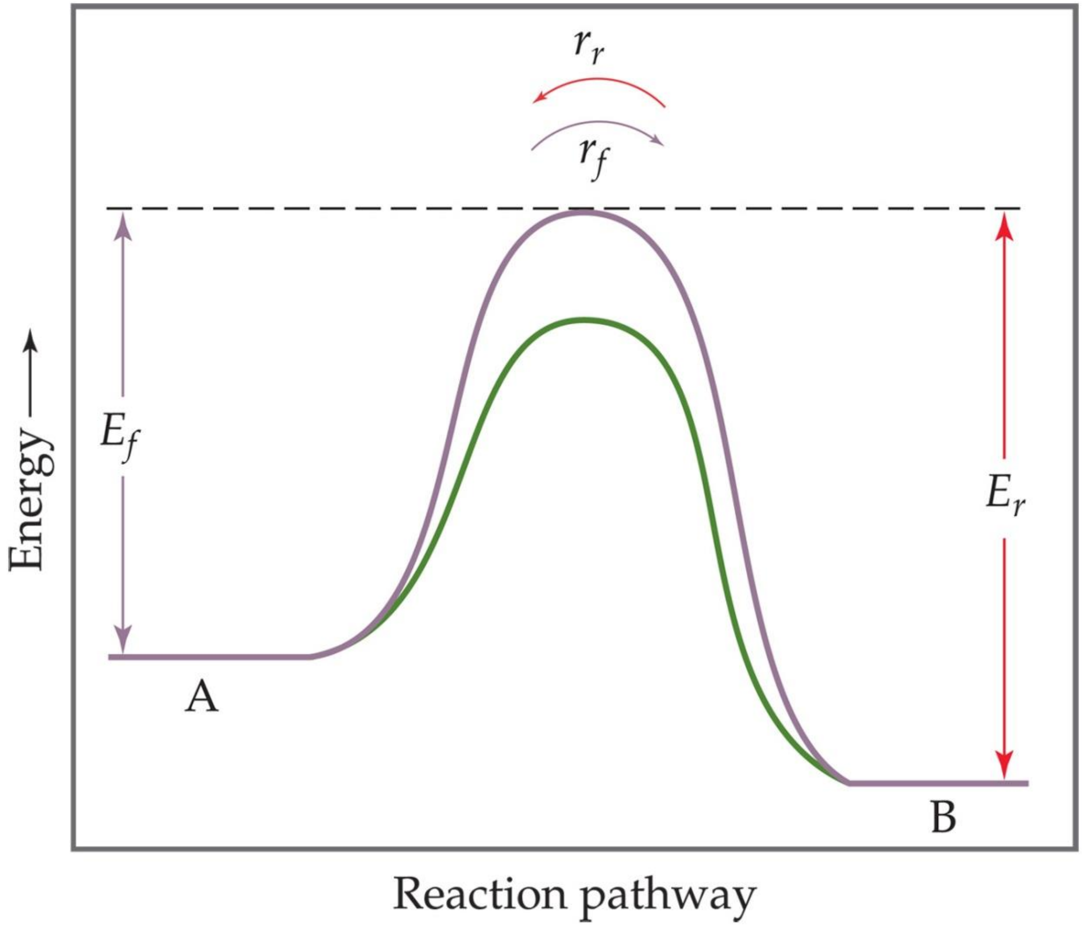
The Effect of Changes in Temperature

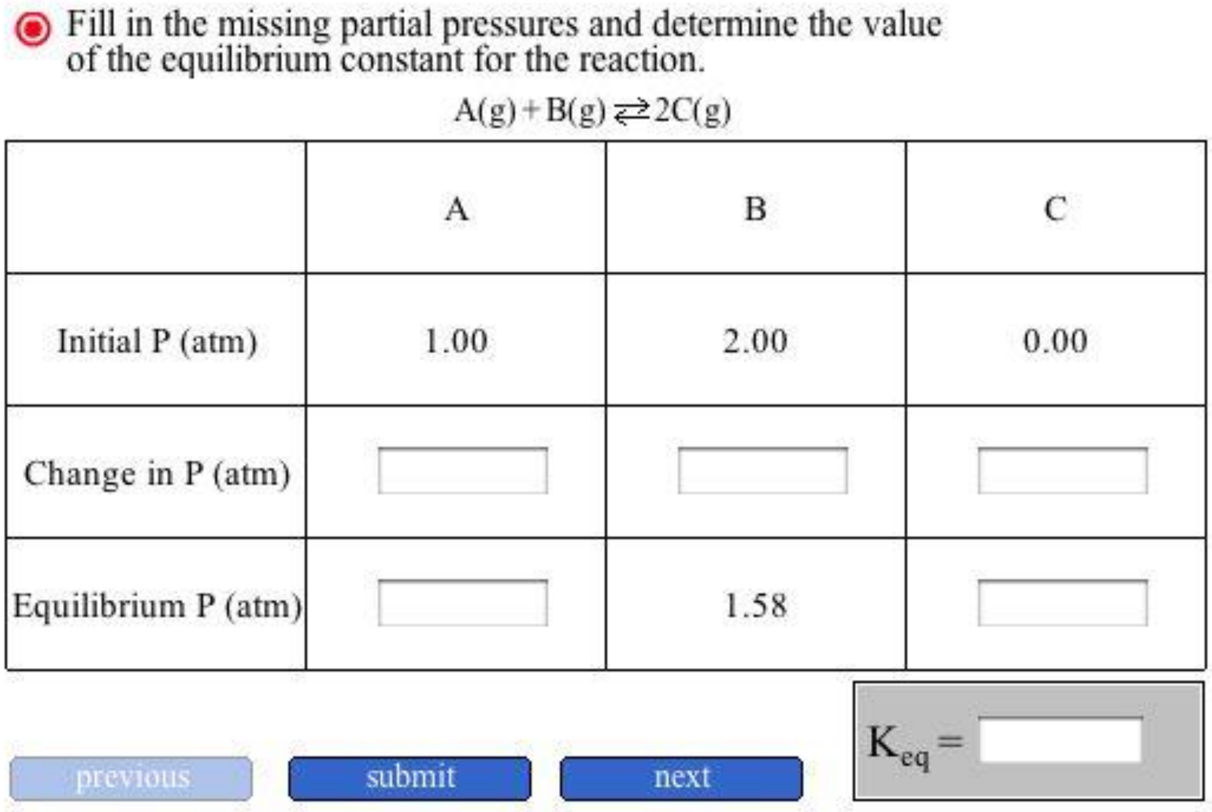


Catalysts increase the rate of both the forward *and* reverse reactions.



Equilibrium is achieved faster, but the equilibrium composition remains unaltered.





◉ Fill in the missing partial pressures and determine the value of the equilibrium constant for the reaction.

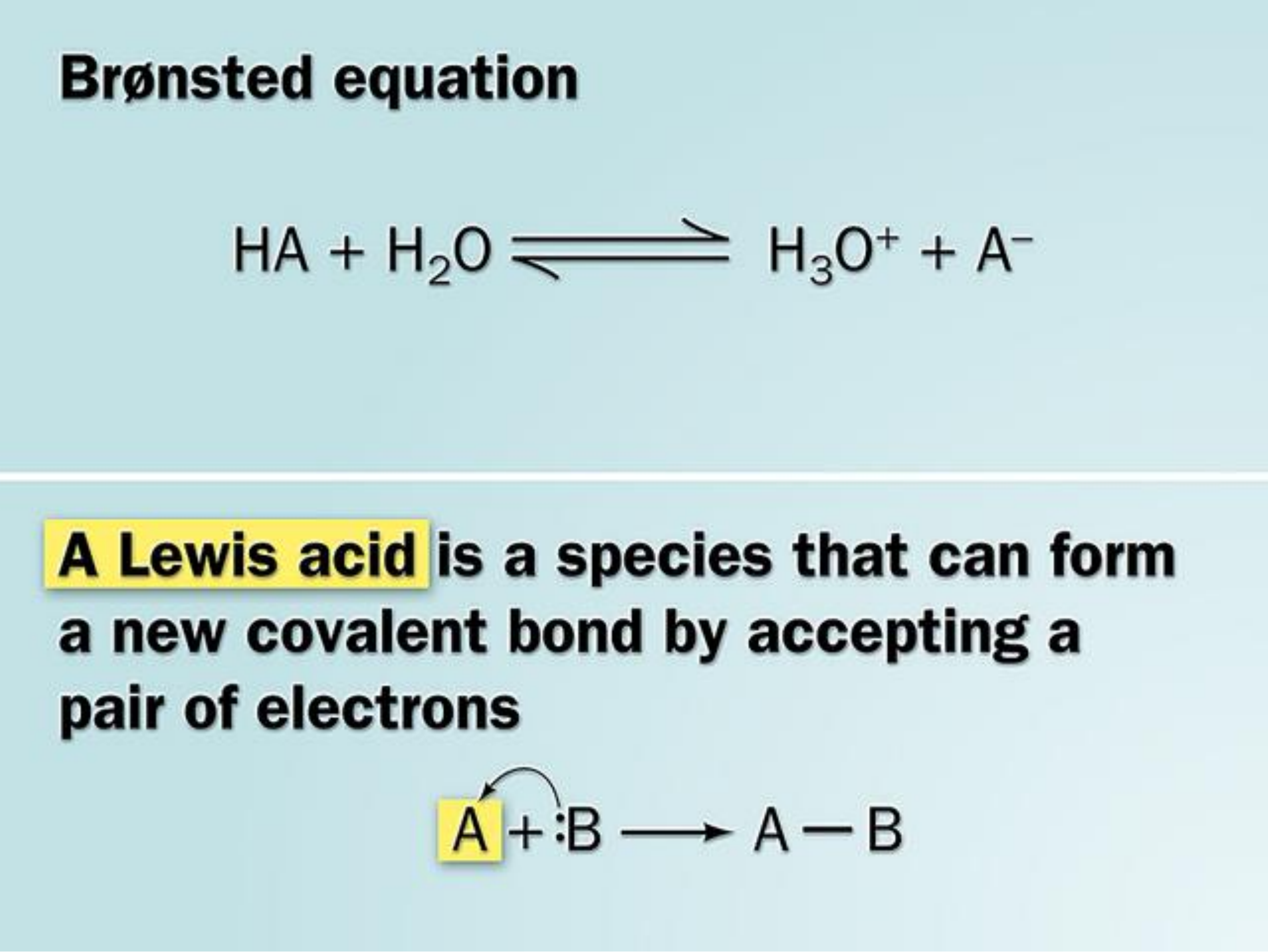
$$A(g) + B(g) \rightleftarrows 2C(g)$$

	A	B	C
Initial P (atm)	1.00	2.00	0.00
Change in P (atm)	☐	☐	☐
Equilibrium P (atm)	☐	1.58	☐

$K_{eq} =$ ☐

Ácidos e Bases

Ácidos e Bases: Definições



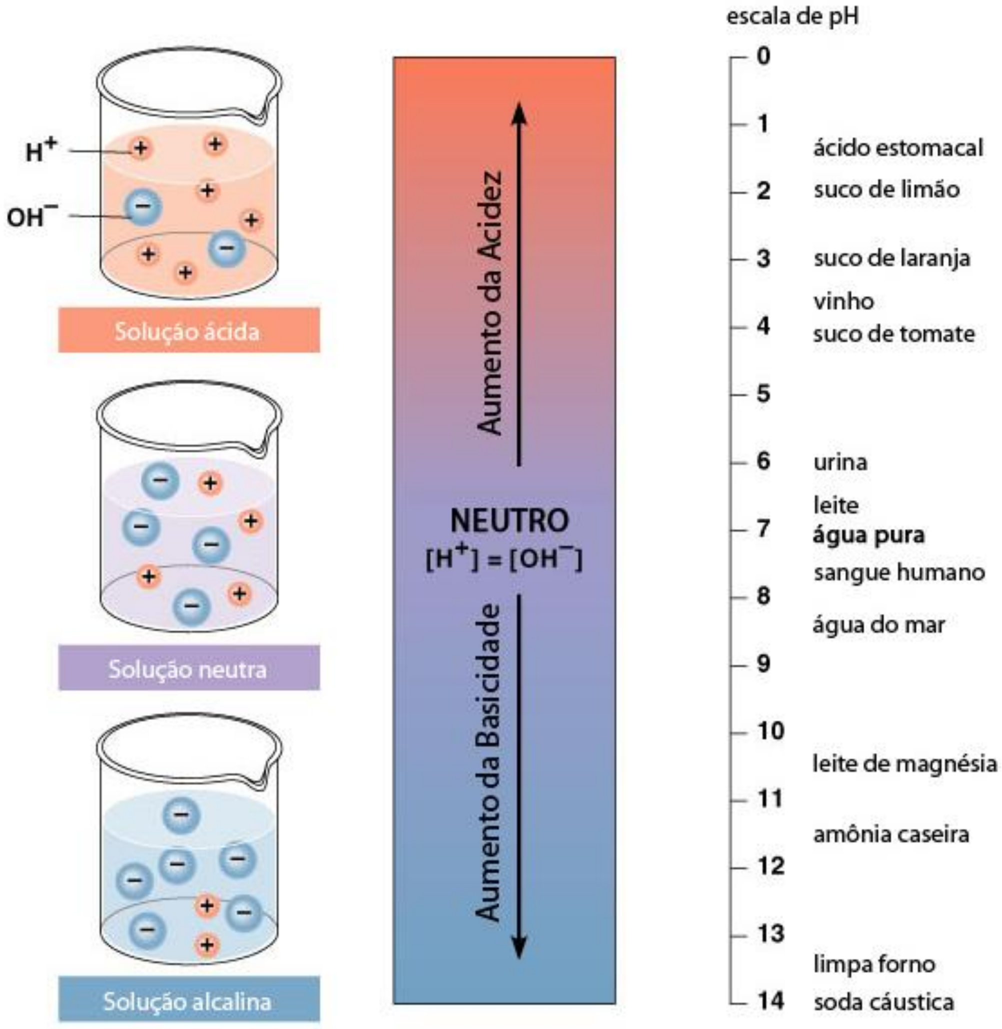
Brønsted equation

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

A Lewis acid is a species that can form a new covalent bond by accepting a pair of electrons

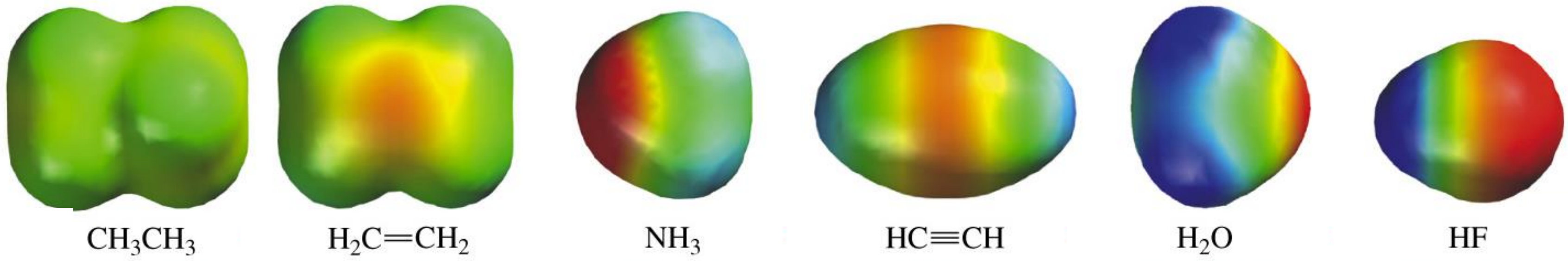
$$A + :B \longrightarrow A{-}B$$

Acidez e Basicidade: pH



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

pK_a: Acidez Relativa



$$\underbrace{\mathrm{HA}}_{\text{Acid}} \rightleftharpoons \mathrm{H}^{+} + \underset{\text{Conjugate base}}{\mathrm{A}^{-}}$$

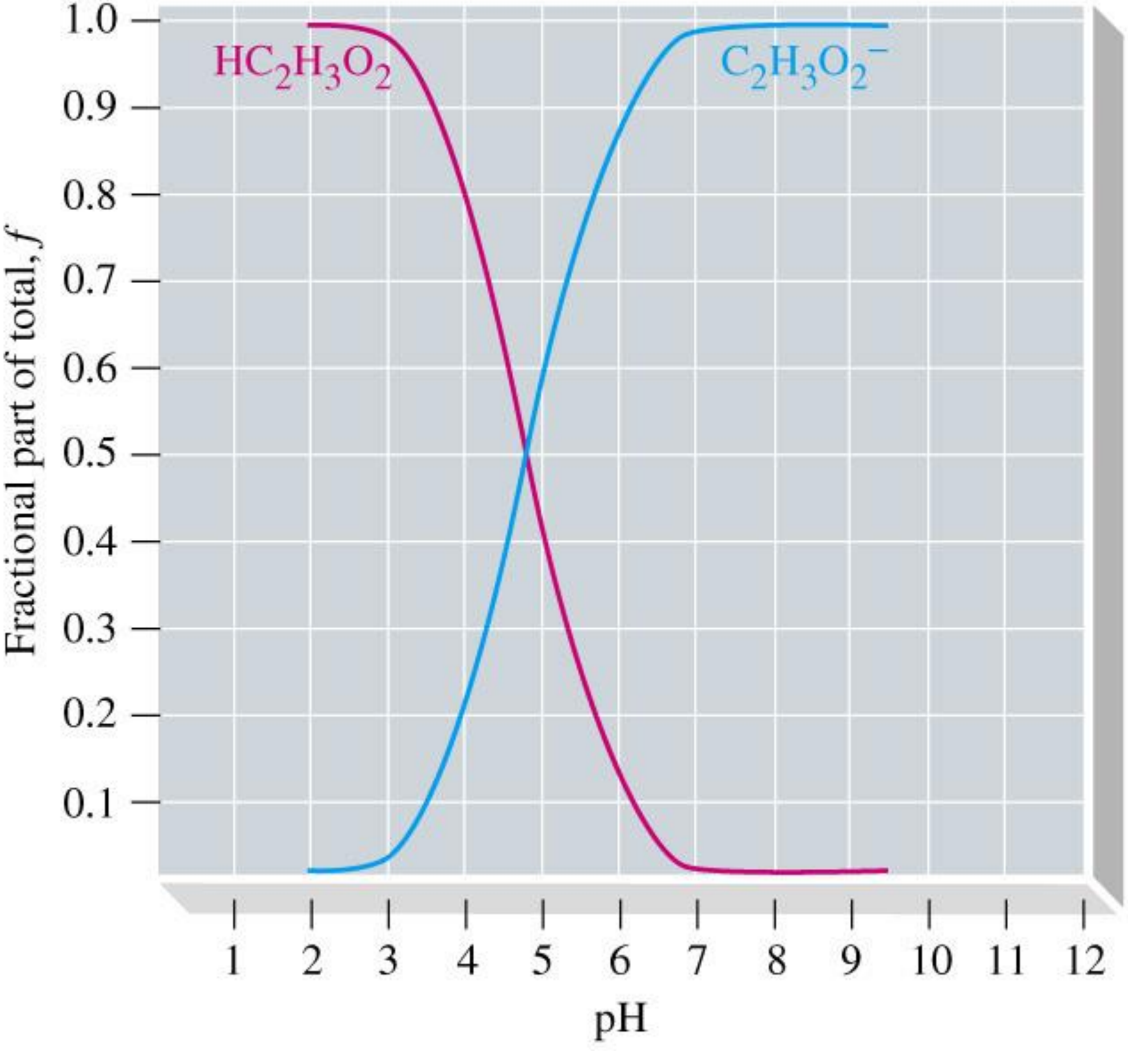
$$K_a = \frac{[\mathrm{H}^{+}][\mathrm{A}^{-}]}{[\mathrm{HA}]}$$

$$\mathrm{p}K_a = -\log K_a$$

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

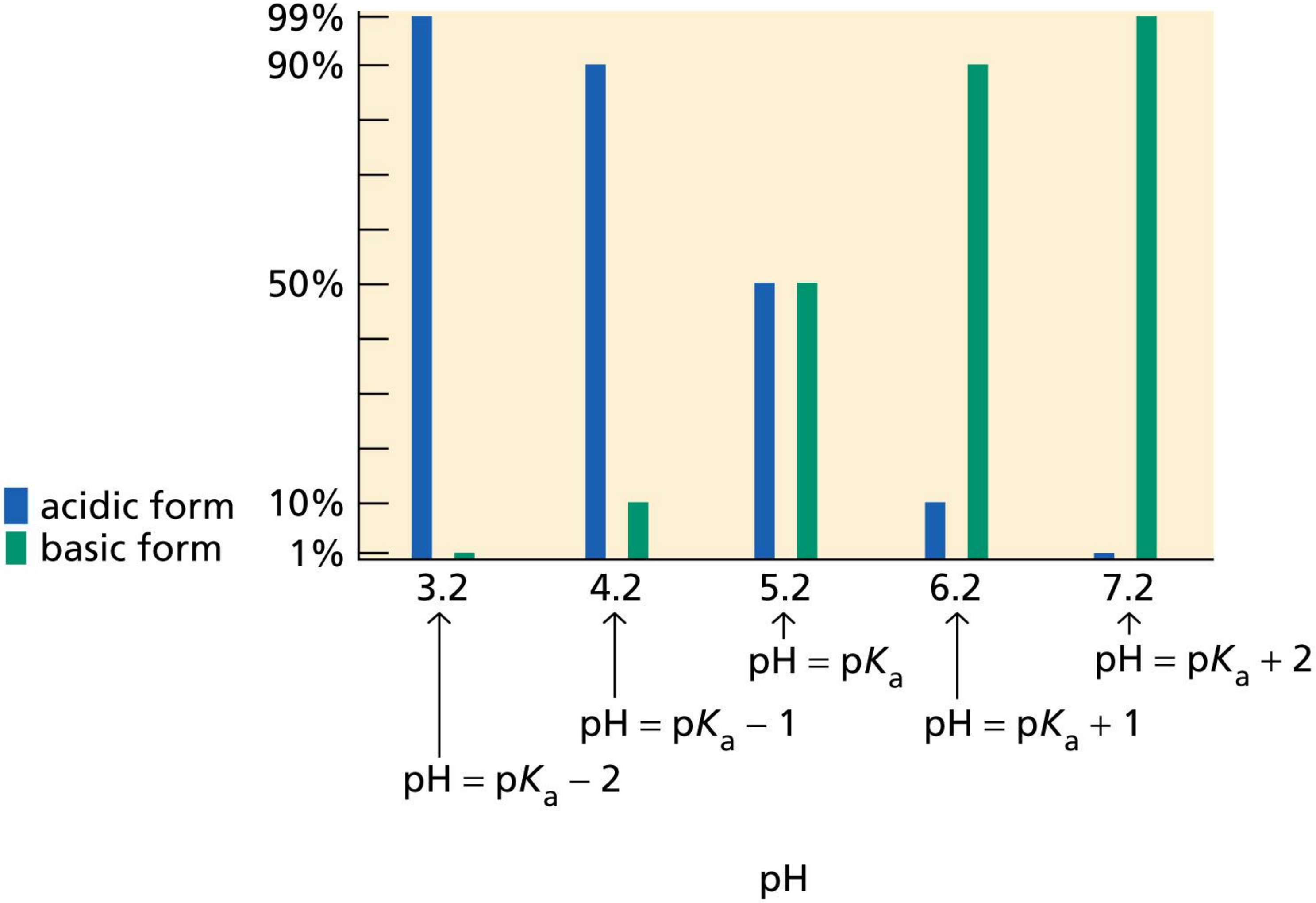
$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log_{10} \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

HA is a weak acid
A^- is its conjugate base
[ ] refers to concentration in moles/l

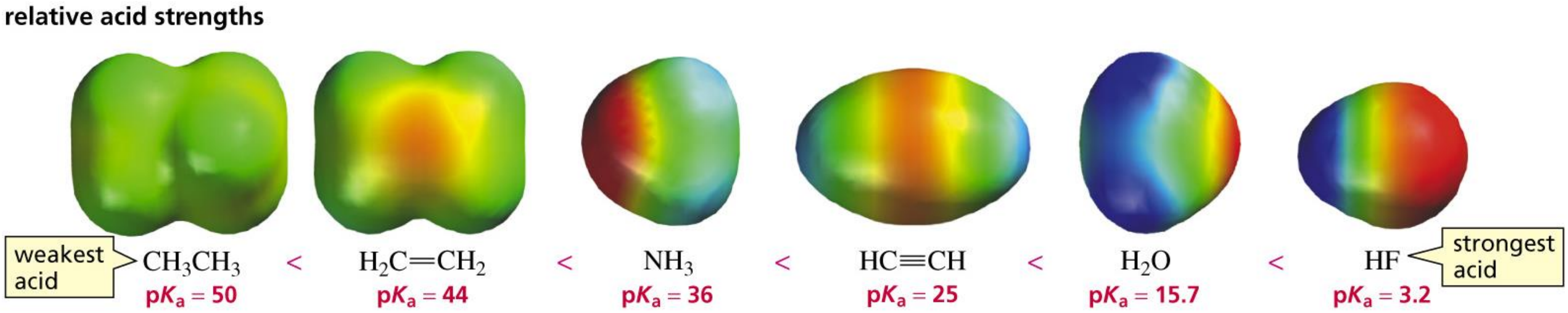


$HC_2H_3O_2$
$C_2H_3O_2^-$
Fractional part of total, f
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
6
7
8
9
10
11
12
pH

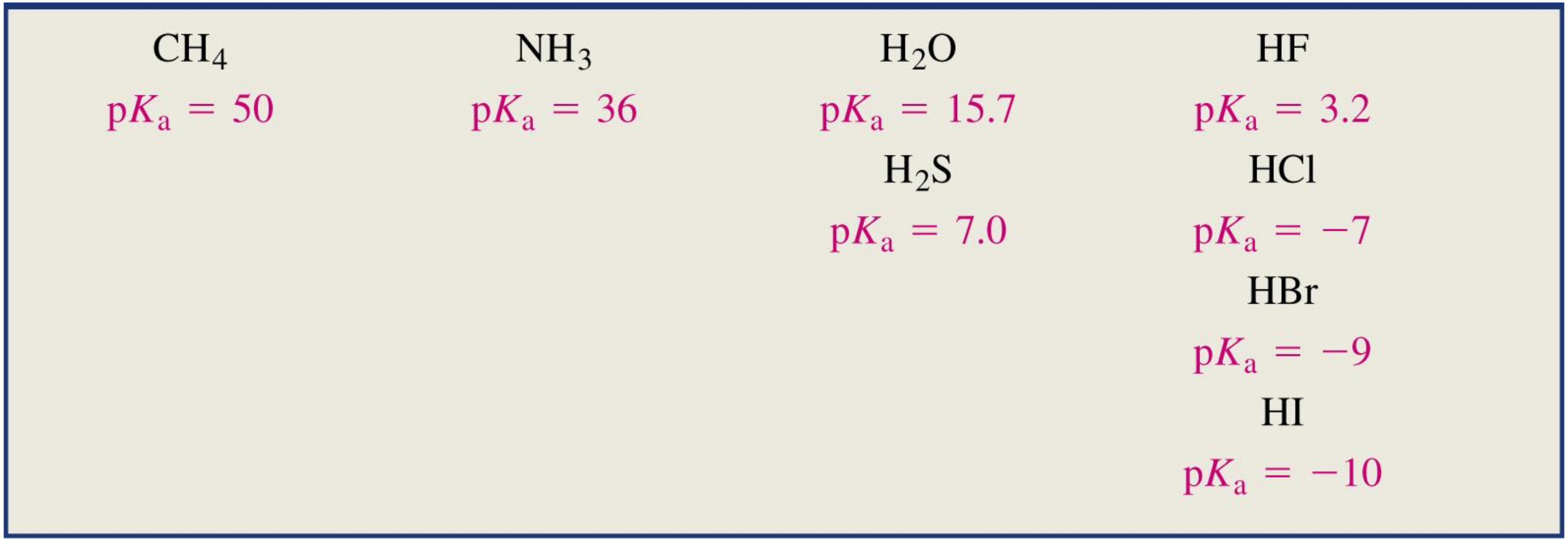
Conceito de pK_a



pK_a: Acidez Relativa



Valores de pK_a



CH_4	NH_3	H_2O	HF
$pK_a = 50$	$pK_a = 36$	$pK_a = 15.7$	$pK_a = 3.2$
		H_2S	HCl
		$pK_a = 7.0$	$pK_a = -7$
			HBr
			$pK_a = -9$
			HI
			$pK_a = -10$

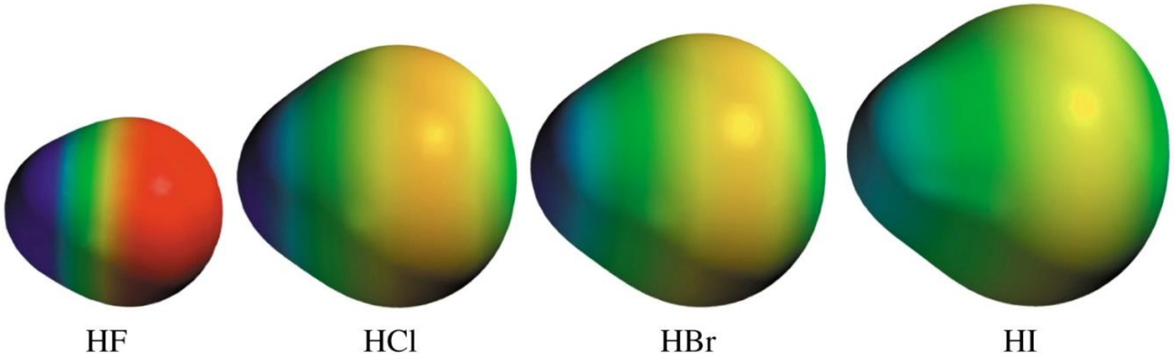
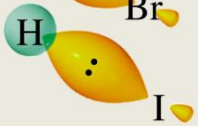
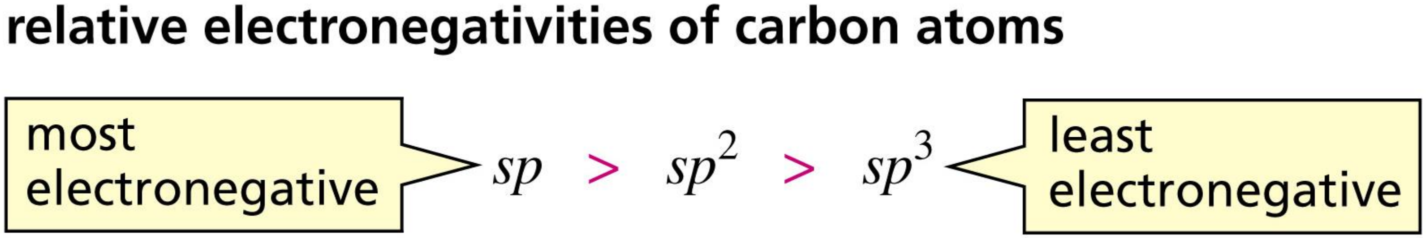


Table 1.6 Hydrogen–Halogen Bond Lengths and Bond Strengths

Hydrogen halide		Bond length (Å)	Bond strength kcal/mol	Bond strength kJ/mol
H—F		0.917	136	571
H—Cl		1.2746	103	432
H—Br		1.4145	87	366
H—I		1.6090	71	298



relative electronegativities of carbon atoms

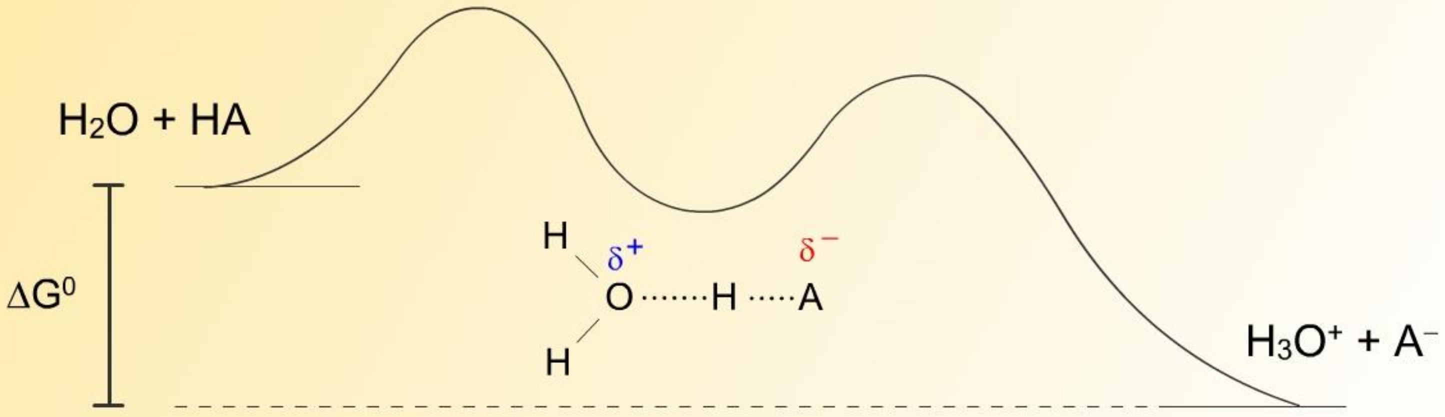
most electronegative $sp > sp^2 > sp^3$ least electronegative

$HC\equiv CH$	$H_2C=CH_2$	CH_3CH_3
$pK_a = 25$	$pK_a = 44$	$pK_a = 50$

$$H_2O + HA \overset{K_{eq}}{\rightleftharpoons} H_3O^+ + A^-$$

$$K_{eq} = \frac{[H_3O^+]\,[A^-]}{[H_2O]\,[HA]}$$

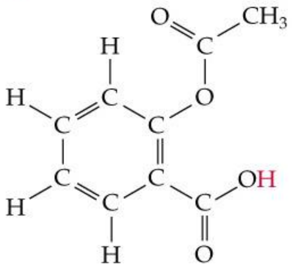
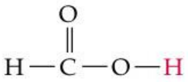
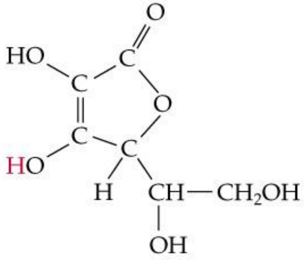
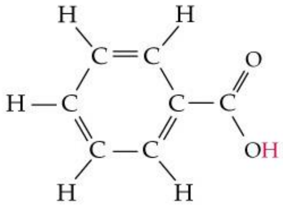
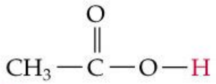
$$K_a = K_{eq}\,[H_2O]$$



$$\Delta G^0 = -RT \ln K_{eq}$$

Acid	**Formula**	**K_a (25°C)**
Acetic	CH_3COOH	1.8×10^{-5}
Chloroacetic	$CH_2ClCOOH$	1.4×10^{-3}
Dichloroacetic	$CHCl_2COOH$	3.3×10^{-2}
Trichloroacetic	CCl_3COOH	2×10^{-1}

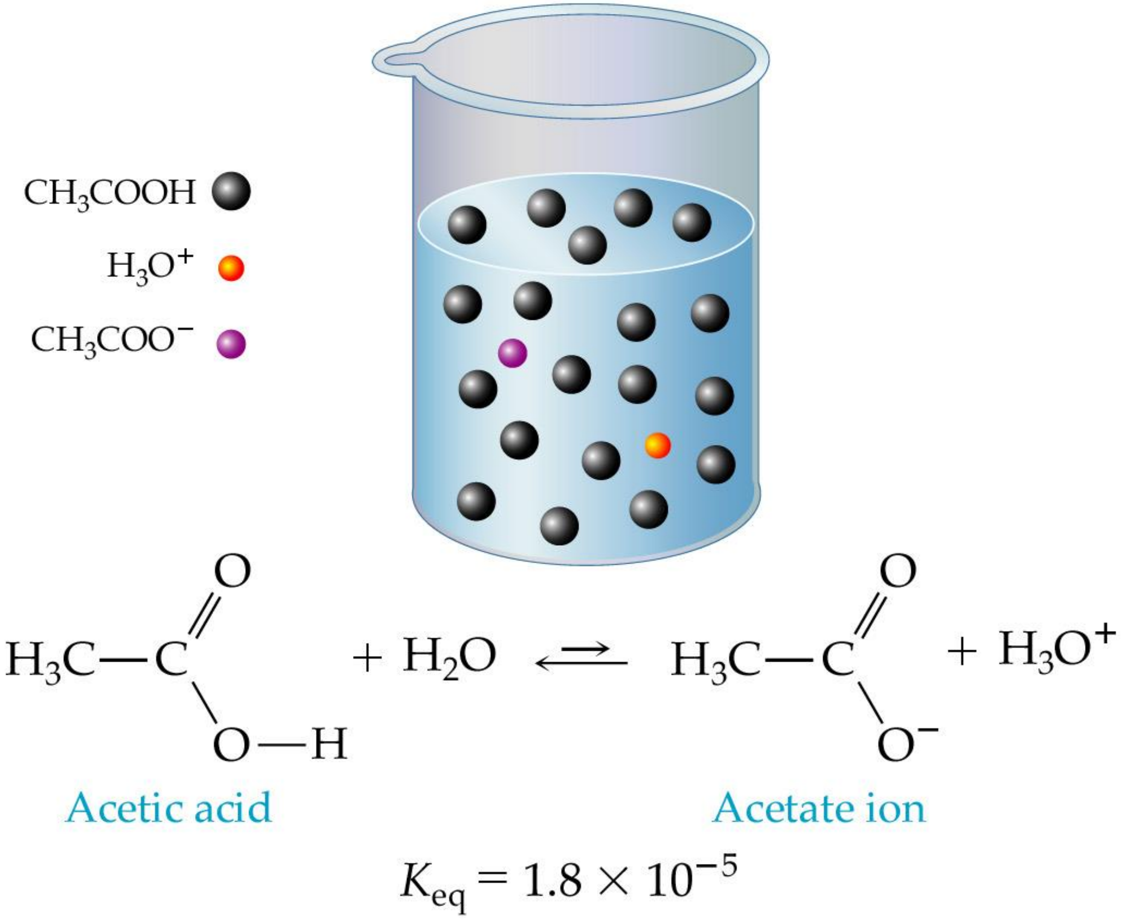
TABLE 15.2 Acid–Dissociation Constants at 25°C

	Acid	Molecular Formula	Structural Formula*	K_a	pK_a†
Stronger acid	Hydrochloric	HCl	$H-Cl$	2×10^{6}	−6.3
	Nitrous	HNO_2	$H-O-N=O$	4.5×10^{-4}	3.35
	Hydrofluoric	HF	$H-F$	3.5×10^{-4}	3.46
	Acetylsalicylic (aspirin)	$C_9H_8O_4$		3.0×10^{-4}	3.52
	Formic	HCO_2H	 $H-\overset{O}{\overset{\Vert}{C}}-O-H$	1.8×10^{-4}	3.74
	Ascorbic (vitamin C)	$C_6H_8O_6$		8.0×10^{-5}	4.10
	Benzoic	$C_6H_5CO_2H$		6.5×10^{-5}	4.19
	Acetic	CH_3CO_2H	 $CH_3-\overset{O}{\overset{\Vert}{C}}-O-H$	1.8×10^{-5}	4.74
	Hypochlorous	$HOCl$	$H-O-Cl$	3.5×10^{-8}	7.46
Weaker acid	Hydrocyanic	HCN	$H-C\equiv N$	4.9×10^{-10}	9.31
	Methanol	CH_3OH	CH_3-O-H	2.9×10^{-16}	15.54

* The proton that is transferred to water when the acid dissociates is shown in color.

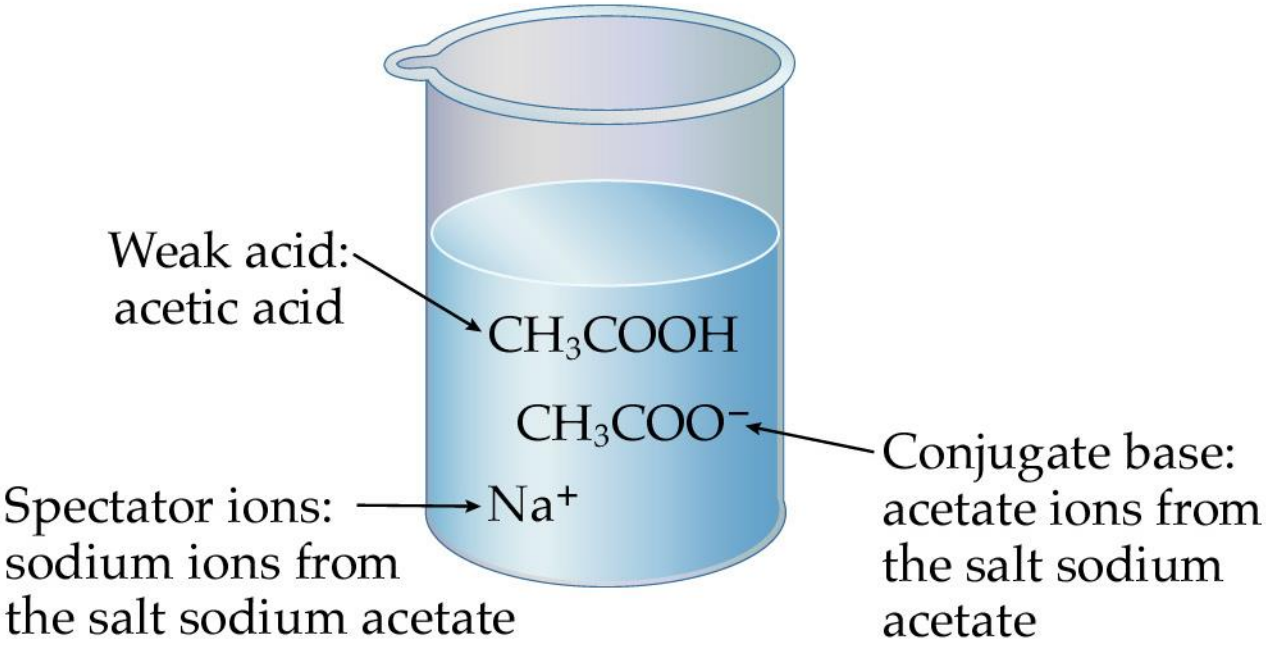
† p$K_a = -\log K_a$.

Tampão Acetato



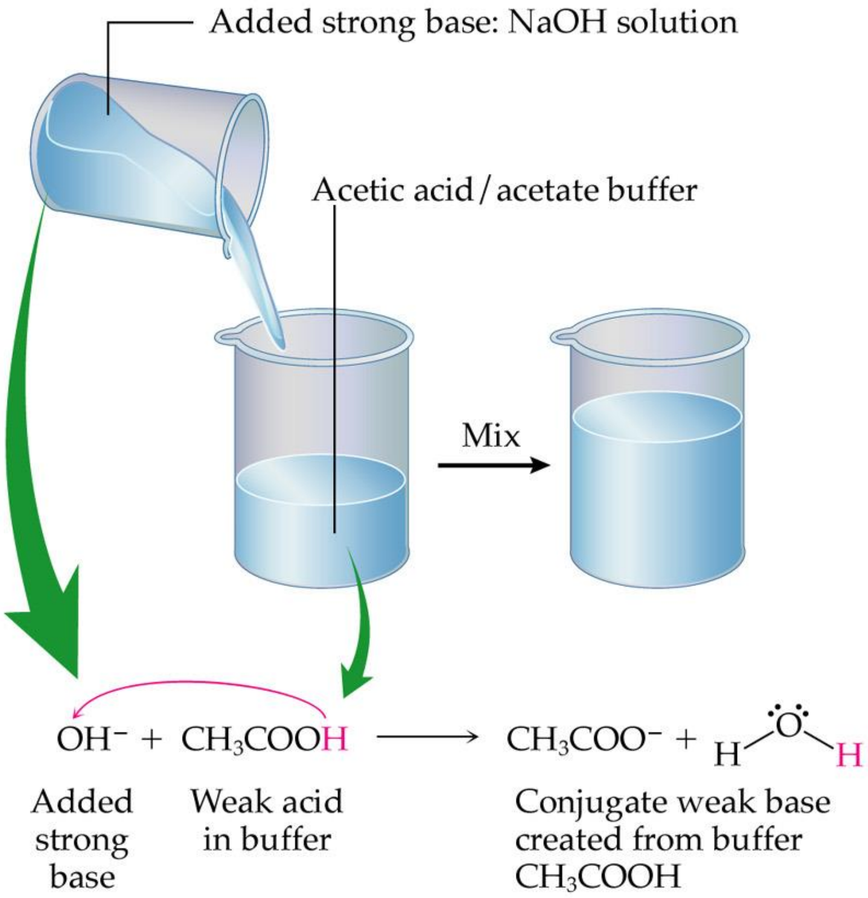
$$K_{eq} = 1.8 \times 10^{-5}$$

Solução Tampão



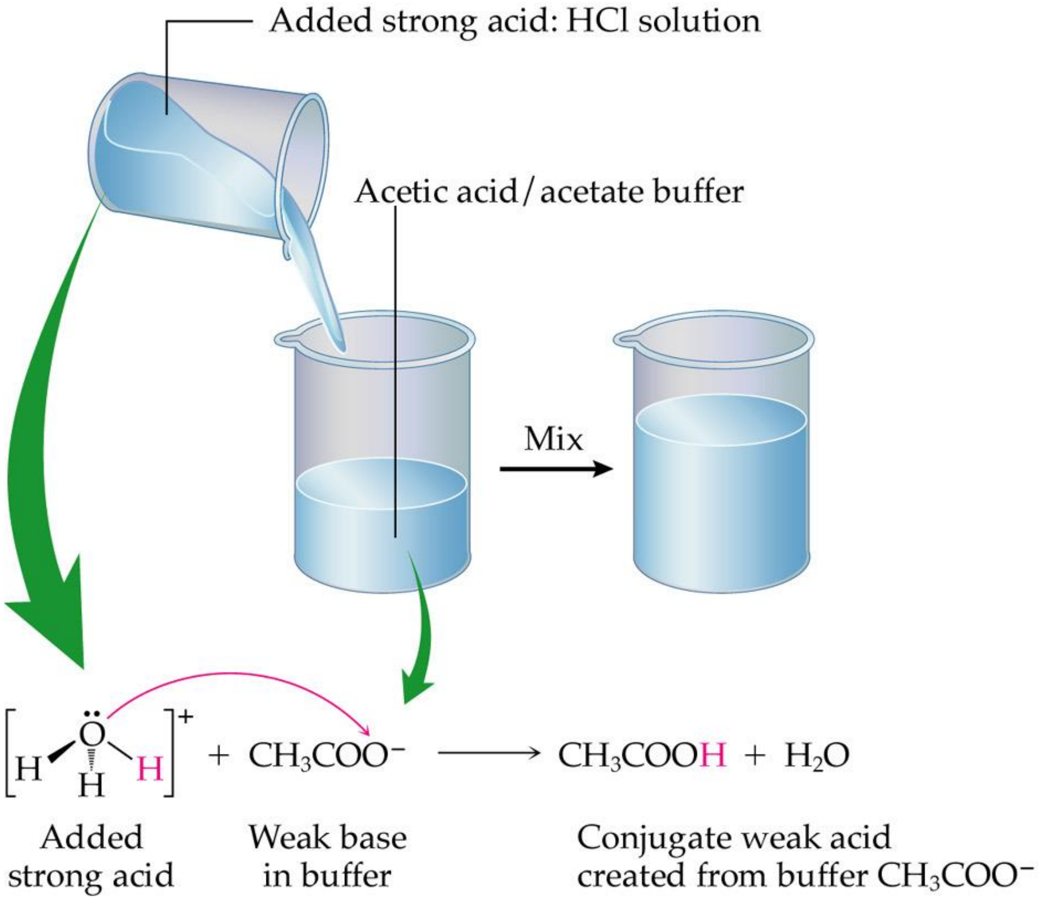
A Buffered Solution

Solução Tampão



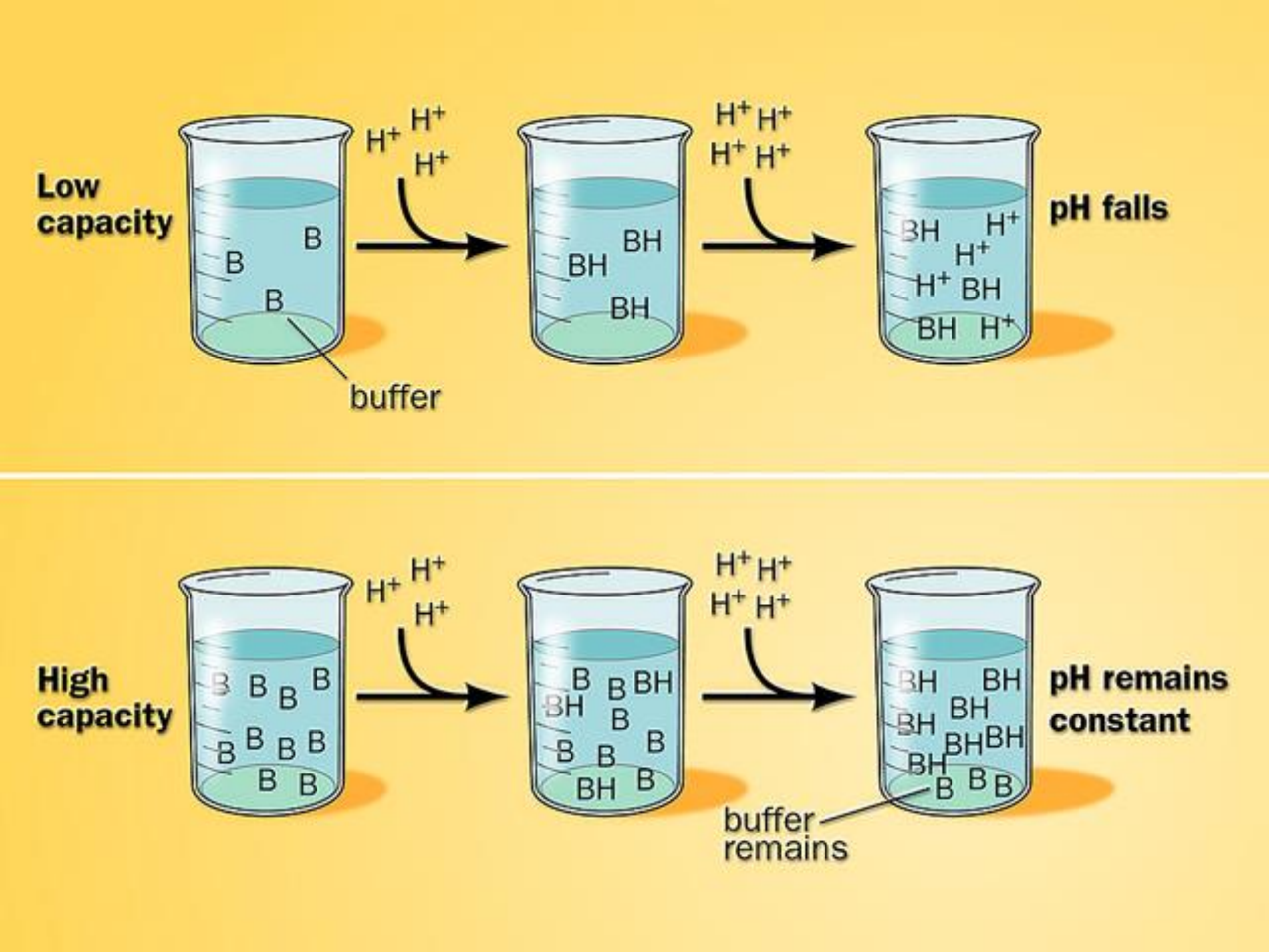
This buffer replaces a strong base with a weak base at the expense of some buffering weak acid.

Solução Tampão

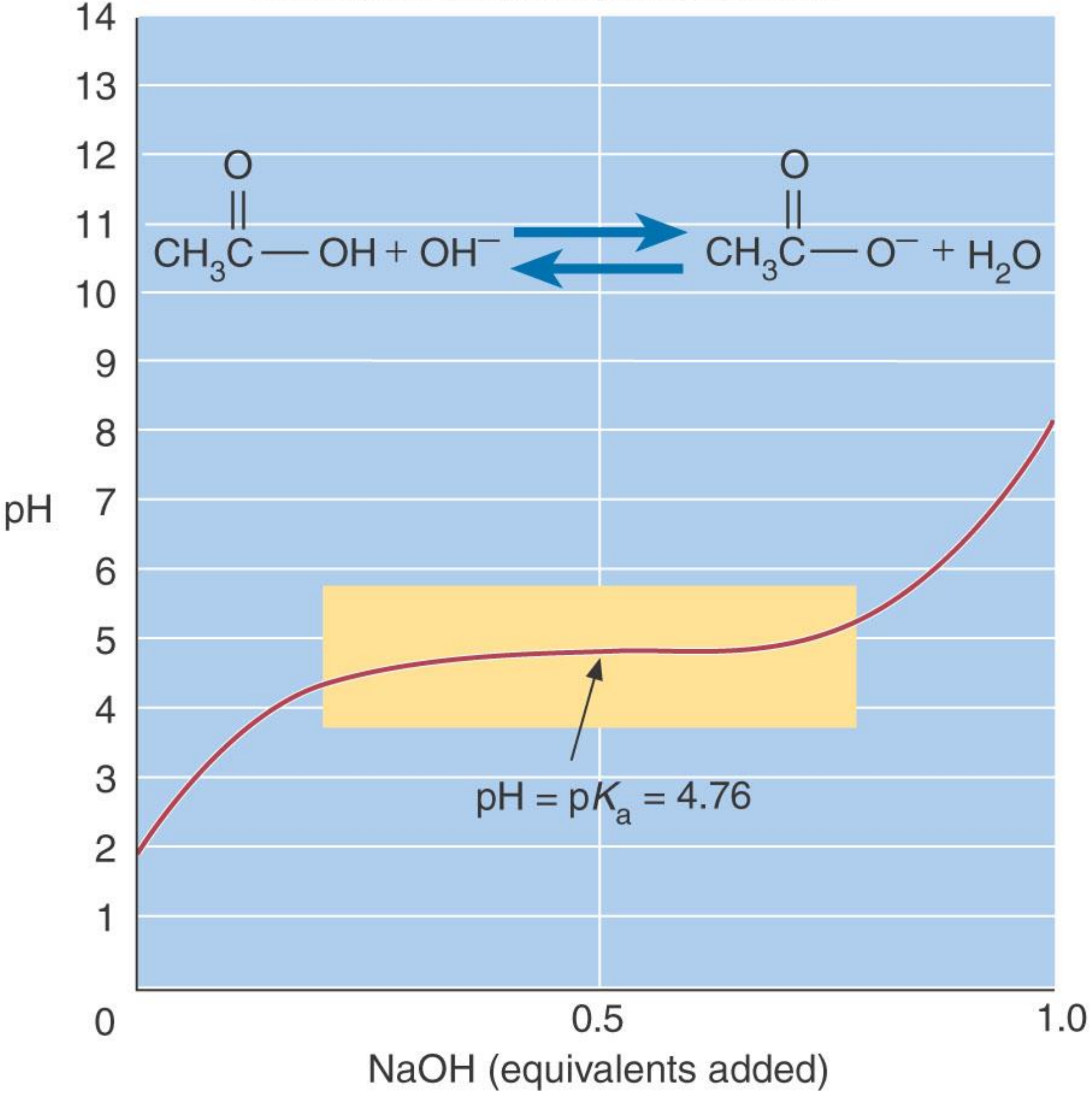


This buffer replaces a strong acid with a weak acid at the expense of some buffering weak base.

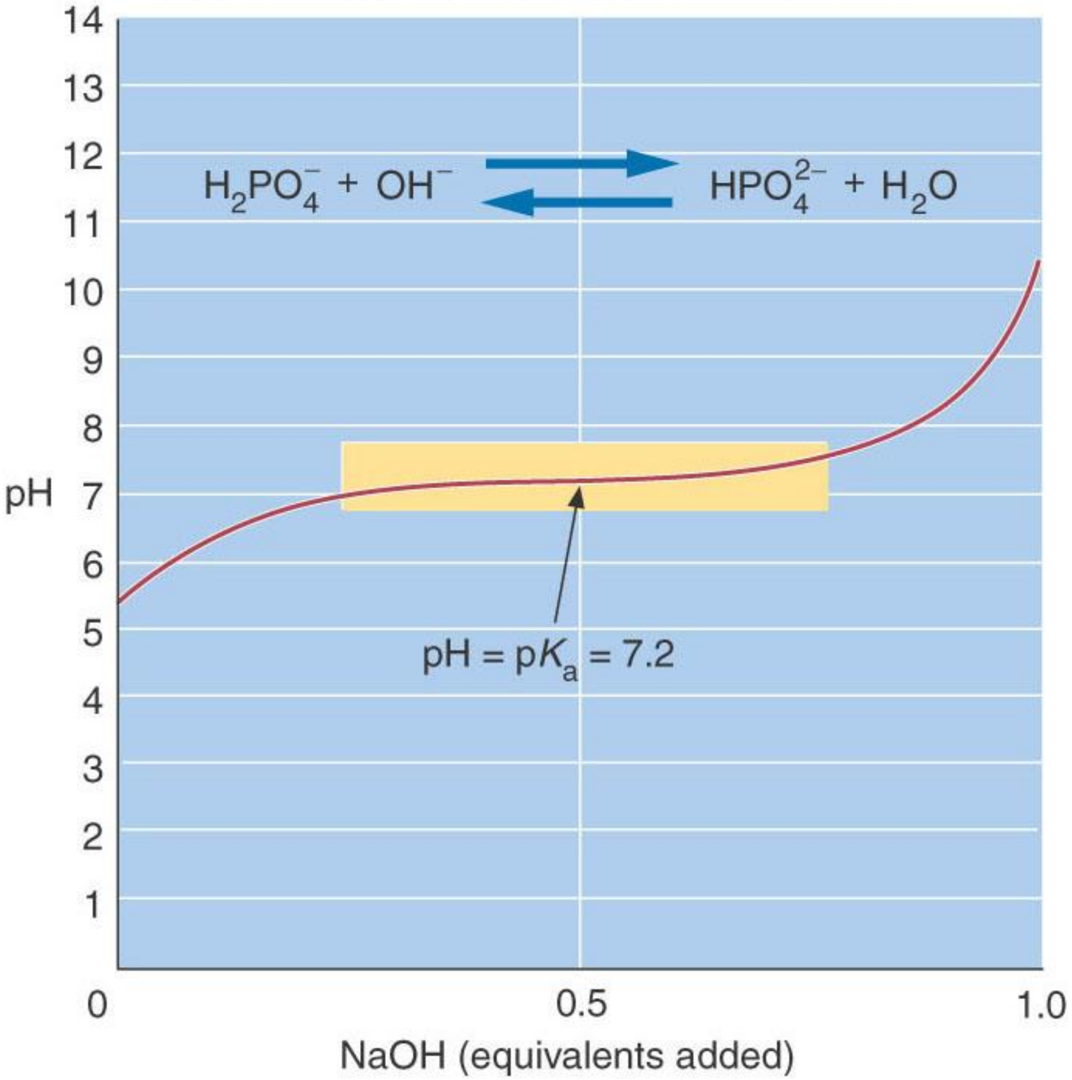
Solução Tampão



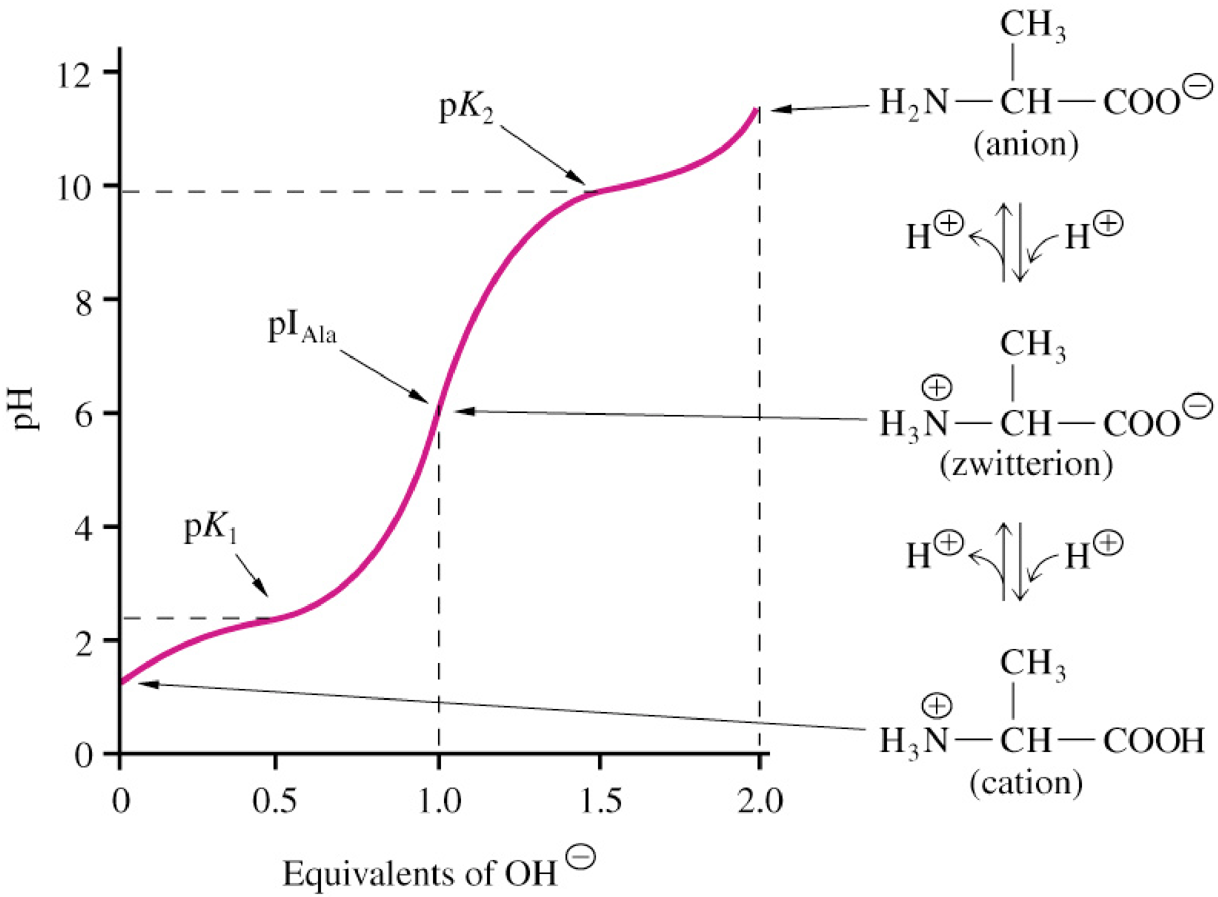
Faixa de Tamponamento



Faixa de Tamponamento



Efeito tamponante

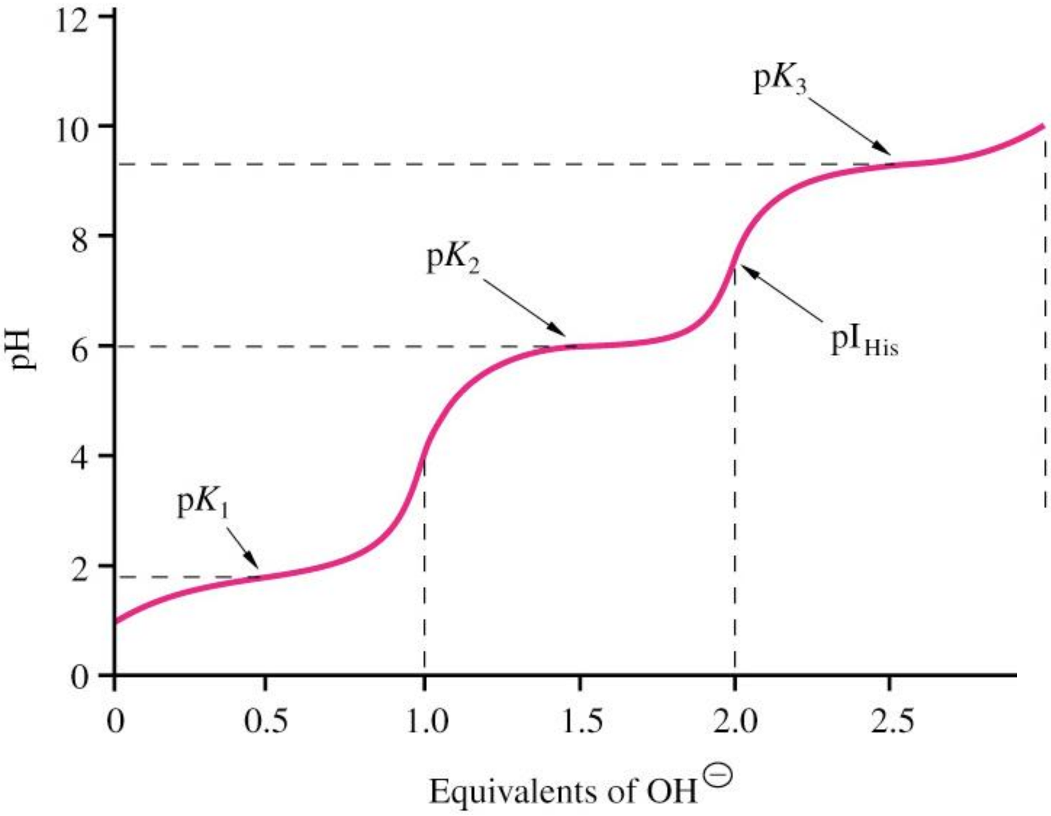


pK_{a1} = 2,4

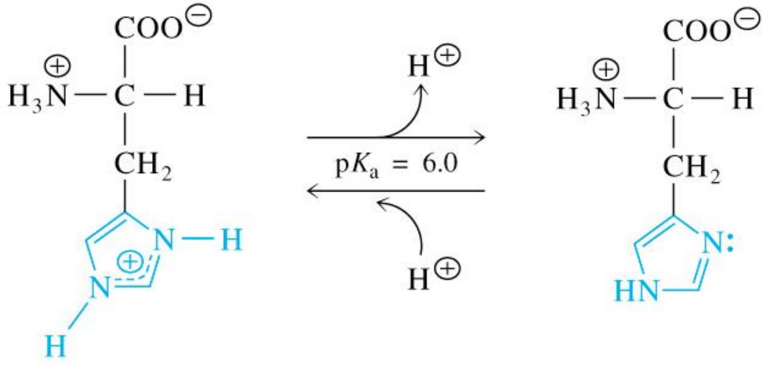
pK_{a2} = 9,9

pI_{Ala} = PI

Faixa de Tamponamento

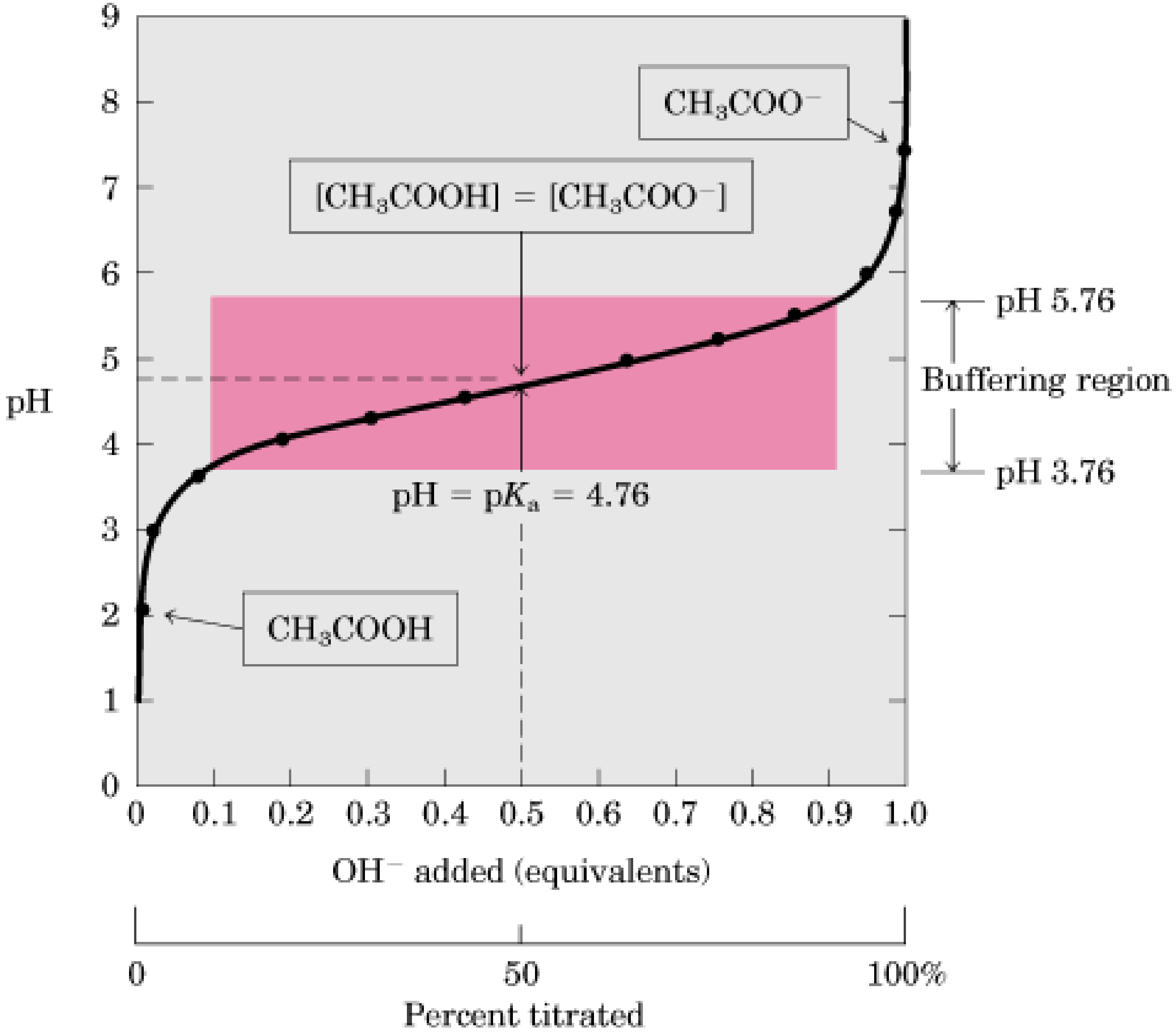


pK_{a1} = 1,8
pK_{a2} = 6,0
pK_{a3} = 9,3

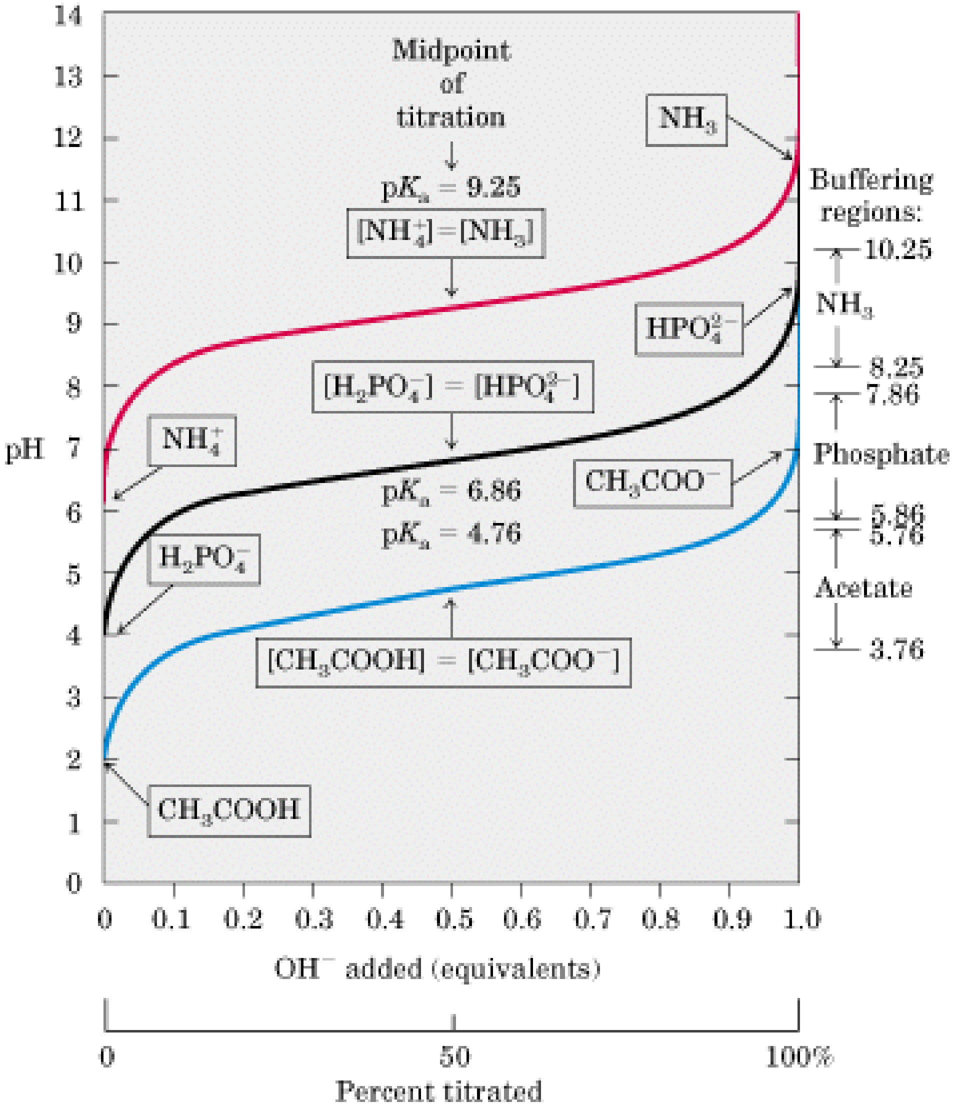


Imidazolium ion
(protonated form)
of histidine side chain

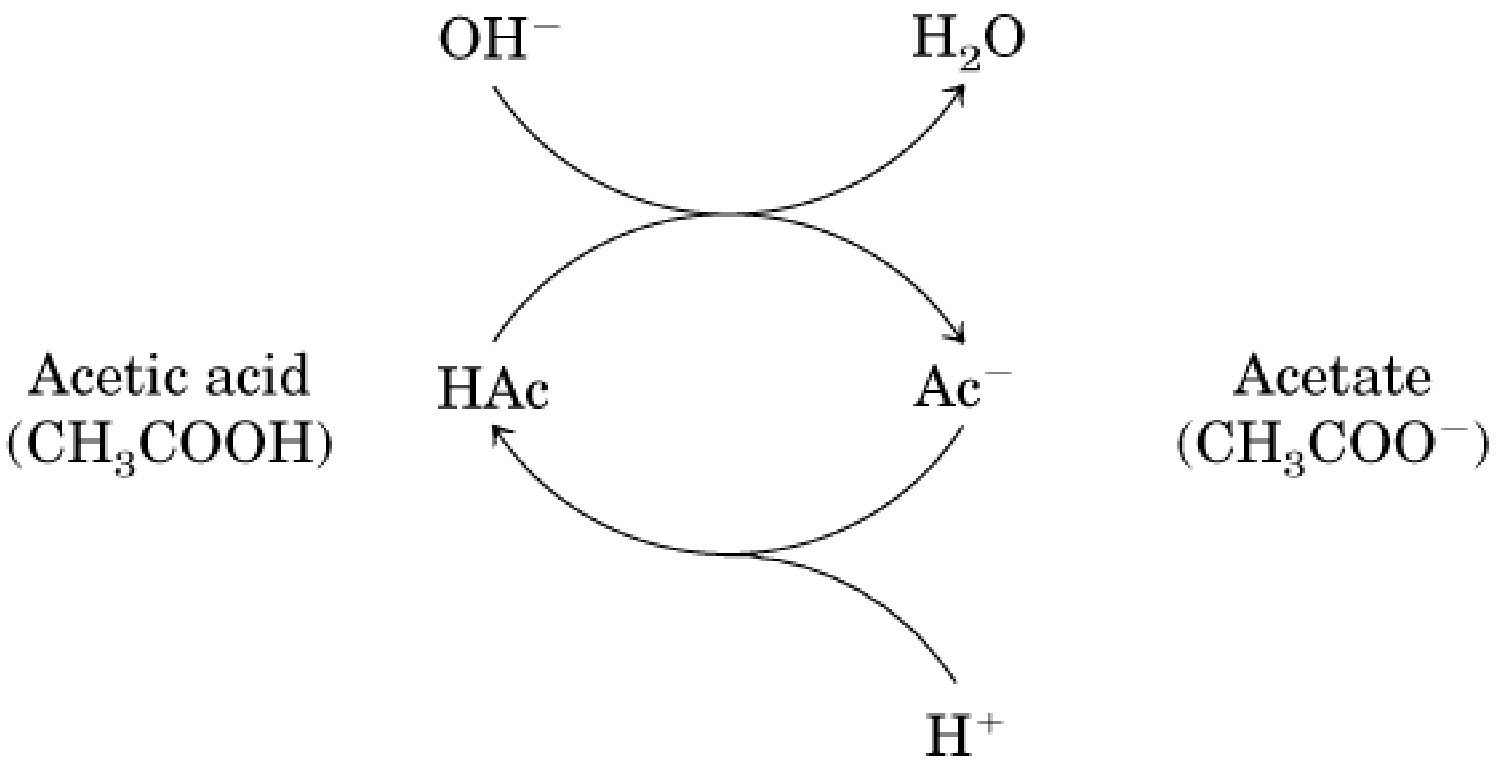
Imidazole
(deprotonated form)
of histidine side chain



CH_3COO^-
$[CH_3COOH] = [CH_3COO^-]$
pH 5.76
Buffering region
pH 3.76
$pH = pK_a = 4.76$
CH_3COOH
pH
9
8
7
6
5
4
3
2
1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
OH^- added (equivalents)
0
50
100%
Percent titrated


Midpoint of titration
$\mathrm{p}K_a = 9.25$
$[NH_4^+] = [NH_3]$
NH_3
Buffering regions:
10.25
NH_3
8.25
7.86
Phosphate
5.86
5.76
Acetate
3.76
HPO_4^{2-}
$[H_2PO_4^-] = [HPO_4^{2-}]$
NH_4^+
$\mathrm{p}K_a = 6.86$
$\mathrm{p}K_a = 4.76$
CH_3COO^-
$H_2PO_4^-$
$[CH_3COOH] = [CH_3COO^-]$
CH_3COOH
pH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
OH^- added (equivalents)
0
50
100%
Percent titrated

$$K_w = [H^+][OH^-]$$



$$K_a = \frac{[H^+][Ac^-]}{[HAc]}$$

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$