Big Idea #6

Equilibrium, Acids & Bases, Titrations, & Solubility

equilibrium constants

$aA + bB \rightleftharpoons cC + dD$

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

large K_{eq} product-favoring

small K_{eq} reactant-favoring

only gases and aqueous species appear in equilibrium expression

↳ K has no units

K_c molar concentrations

K_p partial pressures

K_{sp} solubility product

K_a acid dissociation constant (weak acids)

K_b base dissociation constant (weak bases)

K_w ionization of water ($K_w = 1 \times 10^{-14}$)

changes in equilibrium constant

concentration and pressure changes do not change K_{eq}

increase in temp (shift to left) increases [reactants]

↳ K_{eq} decreases

decrease in temp (shift to right) increases [products]

↳ K_{eq} increases

reaction quotient

$aA + bB \rightleftharpoons cC + dD$

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

$Q < K$ reaction shifts right

$Q > K$ reaction shifts left

$Q = K$ reaction is at equilibrium

voltaic cells

always given at standard conditions (25°C, 1.0 atm)

$K_{eq} >> 1$ (very favored)

voltage = 0 if $Q = K$

reaction quotient (Q) = 1 at standard conditions

Q increases (closer to K) cell potential decreases

Q decreases (further from K) cell potential increases

solubility product (K_{sp})

$A_aB_{b(s)} \rightleftharpoons aA^{b+}_{(aq)} + bB^{a-}_{(aq)}$

$K_{sp} = [A^{b+}]^a[B^{a-}]^b$

molar solubility moles of salt dissolvable in solution

ex) $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

$8.0 \times 10^{-12} = (2x)^2(x)$

$= 4x^3$

$x = [CrO_4^{2-}] = 1.[illegible] \times 10^{-4}$ M molar solubility

$2x = [Ag^+] = 2.6 \times 10^{-4}$ M (tends to increase w/ temp)

↑ concentrations at equilibrium

acids and bases

Arrhenius a substance that ionizes to produce H^+ or OH^- ions

Brønsted-Lowry a substance that donates H^+ (acid) or accepts H^+ (base)

(form a conjugate pair)

amphoteric capable of acting as an acid or a base (i.e. H_2O)

p(anything) = −log(anything)

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

$pOH = -\log[OH^-]$

$pK_a = -\log K_a$

$pK_b = -\log K_b$

strong acids HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4

strong bases LiOH, NaOH, KOH, $Ba(OH)_2$, $Sr(OH)_2$

pH direct from concentration

acid dissociation constant $K_a = \frac{[H^+][A^-]}{[HA]}$

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

$K_w = 1 \times 10^{-14}$ @ 25°C

$K_aK_b = K_w$

$pK_a + pK_b = 14$

greater K_a stronger acid (more dissociation)

greater K_b stronger base (accepts more H^+)

calculating pH

set up K_a equation

plug values into ICE table

plug values and variable (using initial acid concentration) into K_a

solve for $x = [H^+]$ (x is insignificant when [acid] > 100 · K_a)

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

buffers

solution with a very stable pH

weak acid/base + its conjugate - buffer won't form w/ strong acid/base b/c conjugate is very weak

↳ added H^+ ions neutralized by base

↳ added OH^- ions neutralized by acid

more effective at higher concentrations

when [acid] = [base], pH = pK_a

(choose acid w/ pK_a close to desired pH)

indicator changes color when pH = indicator's pK_a

manipulating K_{eq}

(1) flip a reaction → take reciprocal of equilibrium constant

(2) multipy reaction → take equilibrium constant to that power

(3) add two reactions → multiply equilibrium constants

Le Chatelier's principle

stress	shift	why
increase concen.	away from sub.	extra concentration needs to be used up
decrease concen.	towards substance	produce more substance to make up for loss
increase pressure	towards fewer mol of gas	pressure increase = volume decrease
decrease pressure	towards more mol of gas	pressure decrease = volume increase
increase temp	shifts to consume added thermal energy	
decrease temp	shifts to replace removed thermal energy	

adding inert gas at constant pressure

decreases mole fraction of other gases, reducing their part. press.

↳ shift towards more mol of gas

adding inert gas at constant volume

partial pressures of other gases do not change → no shift

adding a catalyst

changes rxn rates, not ratios → no shift

dilution

shifts to side with more aqueous species

common ion effect

more soluble salt causes less soluble salt to precipitate

$[Ag^+] = [Cl^-] = 1.3 \times 10^{-5}$ M

0.1 M NaCl is added

$[Ag^+][Cl^-] = 1.6 \times 10^{-10}$

$[Ag^+][0.1] = 1.6 \times 10^{-10}$

$[Ag^+] = 1.6 \times 10^{-9}$ M → $[Ag^+]$ drastically decreases

AgCl precipitates

free energy & equilibrium constant

$\Delta G^\circ = -RT\ln(K)$

ΔG° = free energy (J/mol)

R = gas constant (8.31 J/mol·K)

T = temperature (K)

K = equilibrium constant

percent dissociation

binary acids with less electronegative atoms "give up" H^+ easily

H–Ö–F̈: H–Ö–B̈r:

F's high electronegativity weakens H-O bond (stronger acid)

lower [acid] → stronger acid (reverse rxn less likely)

polyprotic acids

can give up more than one hydrogen in solution

↳ give up first protons more easily than future protons

(production of protons causes equilibrium to shift left)

neutralization reactions

strong acid + strong base both dissociate completely

ex) $HCl + NaOH \rightleftharpoons NaCl + H_2O$

NIE: $H^+ + OH^- \rightleftharpoons H_2O$

strong acid + weak base strong acid donates proton to base

ex) $HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$

NIE: $H^+ + NH_3 \rightleftharpoons NH_4^+$

weak acid + strong base strong base accepts proton

ex) $HC_2H_3O_2 + NaOH$

NIE: $HC_2H_3O_2 + OH^- \rightleftharpoons C_2H_3O_2^- + H_2O$

weak acid + weak base acid gives proton to base

ex) $HC_2H_3O_2 + NH_3$

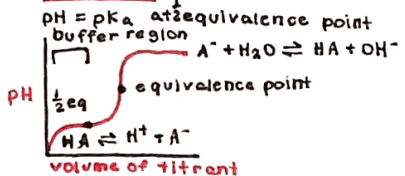
NIE: $HC_2H_3O_2 + NH_3 \rightleftharpoons C_2H_3O_2^- + NH_4^+$

strong base in excess (or acid) use $[OH^-]$ or $[H^+]$ to find pH

weak base in excess (or acid) $pH = pK_a + \log\frac{[A^-]}{[HA]}$

$pOH = pK_b + \log\frac{[HB^+]}{[B]}$

titrations



strong acid, strong base equiv pt. @ 7

strong acid, weak base equiv pt. < 7

weak acid, strong base equiv pt. > 7

weak acid, weak base equiv pt. @ 7

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