

TOPIC 5: Equilibrium reactions

Free energy and equilibrium Experimental approach to Kc and Kp

Relation between Kc and Kp Heterogeneous equilibrium Le Chatelier's principle

Acids and bases Self-ionization of water pH, pOH and pK Strength of acids and bases Polyprotic acids Conjugated acids and bases Hydrolysis Buffers Titration and indicators Solubility Bio-connections

Oxidation and reduction. Concepts Balancing oxidation-reduction reactions Electrochemical cells Galvanic cells Electrode potentials and free energy Nersnt equation Electrolytic cells





Free energy and equilibrium

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Gases

$$\widetilde{G}_i - \widetilde{G}_i^0 = RT \ln \frac{P_i}{P_i^0} = RT \ln P_i$$

This is the free energy change to carry gas i (in a mixture) from a reference state (P_i°) to another state P_i .

$$\Delta \widetilde{G} = \Delta \widetilde{G}^0 + RT \ln \frac{P_C^c P_D^a}{P_A^a P_B^b}$$

This is the reaction free energy change in a reaction between gases.

 $\Delta \widetilde{G}^0 = -RT \ln K_P$

This is the relation between free energy change and equilibrium constant in a reaction between gases



Solutes in solutions

It can be demonstrated

$$\widetilde{G}_i - \widetilde{G}_i^0 = RT \ln \frac{P_i}{P_i^0} = RT \ln \{a_i\}$$

This is the free energy change to carry solute i (in a solution with more solutes) from a reference state (P_i°) to another state P_i . The reference state of a solute in a solution is different than for a gas. The quotient P_i / P_i° is called activity, $\{a_i\}$ (dimensionless).

For a general equilibrium reaction where reactants and products are in solution $aA_{(solution)} + bB_{(solution)} \rightarrow cC_{(solution)} + dD_{(solution)}$

$$\Delta \widetilde{G} = \Delta \widetilde{G}^0 + RT \ln \frac{\{C\}^c \{D\}^c}{\{A\}^a \{B\}^b}$$

If all species behave as ideal and the concentration is low enough, then the reaction free energy can be expressed in terms of molarity instead of activity.

$$\Delta \widetilde{G}^{0} = -RT \ln \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} = -RT \ln K_{C}$$
 Equilibrium constant only depends on T



Experimental approach to Kc or Kp

 $CH_3OH(g) \Leftrightarrow CO + 2H_2(g)$

Initial state

	$CH_{3}OH$	СО	H_{2}
exp 1	0 <i>mol</i>	1mol	1mol
exp 2	1mol	0 <i>mol</i>	0mol
exp 3	1mol	1mol	1mol

Equilibrium state

	$CH_{3}OH$	CO	H_{2}
exp 1	0.08 <i>mol</i>	0.95 <i>mol</i>	0.80 <i>mol</i>
exp 2	0.24 <i>mol</i>	0.80 <i>mol</i>	1.50 <i>mol</i>
exp 3	0.60 <i>mol</i>	1.40 <i>mol</i>	1.80 <i>mol</i>



Equilibrium Constant:

$$K_{C} = \frac{\left[CO\right]_{EQ}\left[H_{2}\right]_{EQ}^{2}}{\left[CH_{3}OH\right]_{EQ}} = 7.6$$



Equilibrium constant values

$$aA + bB \Leftrightarrow cC + dD$$

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

All concentrations correspond to Equilibrium concentrations

If K > 1

Equilibrium will shift to the right (product formation). Favorable reaction.

 $\Delta \widetilde{G}^0 < 0$

If K < 1

Equilibrium will shift to the left (reactants formation). Unfavorable reaction.

 $\Delta \widetilde{G}^0 > 0$



Relation between Kp and Kc

Consider a general reaction: $aA + bB \Leftrightarrow cC + dD$

$$P_{i}V = n_{i}RT; \quad \frac{n_{i}}{V} = [C_{i}] = \frac{P_{i}}{RT}; \quad P_{i} = RT[C_{i}]$$

$$K_{p} = \frac{p_{C}^{c} \cdot p_{D}^{d}}{p_{A}^{a} \cdot p_{B}^{b}} \qquad K_{p} = \frac{[C]^{c}(RT)^{c} \cdot [D]^{d}(RT)^{d}}{[A]^{a}(RT)^{a} \cdot [B]^{b}(RT)^{b}}$$

$$K_{p} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \cdot (RT)^{(c+d)-(a+b)}$$

$$K_{C} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \qquad K_{p} = K_{C} \cdot (RT)^{\Delta n}$$

$$\Delta n = (c+d) - (a+b)$$



Heterogeneous equilibrium

When one or more species are not in the same phase (aggregation state)

Let us assume:

$$aA(s) + bB(g) \Leftrightarrow cC(l) + dD(g)$$



Activity of a pure solid or liquid is 1 because reference state is the solid state

$$K_{C} = \frac{\left[C\right]^{c}\left[D\right]^{d}}{\left[A\right]^{a}\left[B\right]^{b}} = \frac{\left[D\right]^{d}}{\left[A\right]^{a}}$$
$$K_{P} = \frac{p_{D}^{d}}{p_{B}^{b}}$$

$$K_P = K_C (RT)^{(d-b)}$$



Le Châtelier's principle

If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.



Concentration:

$$SO_2 + \frac{1}{2}O_2 \Leftrightarrow SO_3 \qquad K_P = \frac{P_{SO_3}}{P_{SO_2}P_{O_2}^{1/2}}$$

Let us add a small quantity of SO_3 , the instantaneous concentration quotient Q before a new equilibrium is established will be





Concentration. Heterogeneous equilibriums

Let us assume a precipitation equilibrium such as

$$BaSO_4(s) \Leftrightarrow Ba_{(ac)}^{2+} + SO_{4(ac)}^{2-}$$
$$K_C = [Ba^{2+}]_{eq} [SO_4^{2-}]_{eq}$$

 \dot{c} What happens if a small quantity of Na₂SO₄ is added?

Before equilibrium is established

$$Q = [Ba^{2+}][SO_4^{2-}] > K_C$$

The system will evolve decreasing SO_4^{2-} and Ba^{2+} concentrations. So Barium sulphate will precipitate



Pressure and volume

Not very important in condensed phases but very important in gases

Let us assume:
$$aA \Leftrightarrow bB$$
 $K_P = \frac{P_B^{\ b}}{P_A^{\ a}} = \frac{(x_B P_T)^b}{(x_A P_T)^a} = \frac{x_B^b}{x_A^a} \times P_T^{\ b-a} = K_x P_T^{\Delta n}$

- If a = b $\Delta n = 0$ the equilibrium is independent on pressure changes
- If a > b An <0; If P_T increases, K_x must increase to keep K_P constant. Reaction shifts to the right





Inert gas addition without volume change

Let us assume: $aA \Leftrightarrow bB$ and we add an inert gas (He) which increases pressure If we mechanically apply the equation $K_P = K_{T}P_T^{\Delta n}$ we will be in error.

Before addition, $P_A + P_B = P_T$; $x_A + x_B = 1$.

After addition partial pressures of A and B does not change, only total pressure. Since there is no change in partial pressures, K_P remains unaltered.



Temperature

Equilibrium constant only depends on temperature

$$-\Delta G_R^0 = RTLnK$$

But for a given reaction at constant T and P $\Delta G^0 = \Delta H^0 - T \Delta S^0$ where ΔH^0 y ΔS^0 are the reaction entropy and enthalpy respectively

$$LnK = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

If in a given temperature range (T_1, T_2) entropy and enthalpy does not change appreciably

$$LnK_{1} = -\frac{\Delta H^{0}}{RT_{1}} + \frac{\Delta S^{0}}{R}$$

$$LnK_{2} = -\frac{\Delta H^{0}}{RT_{2}} + \frac{\Delta S^{0}}{R}$$

$$Ln\frac{K_{2}}{K_{1}} = -\frac{\Delta H^{0}}{R} \left(\frac{1}{T_{2}} - \frac{1}{T_{1}}\right)$$

Endothermic $\Delta H > 0$: if T \uparrow , shifts to the right



Exercise

Calculate the equilibrium constant and its temperature dependence for the water self ionization reaction

 $H_2O_{(l)} \Leftrightarrow H^+{}_{(ac)} + OH^-{}_{(ac)}$

Knowing		∆G ⁰ _f (kJ/ mol) a 298.15 K	∆H ⁰ _f (kJ/ mol) a 298.15 K	
	H ₂ O(I)	-237.178	-285.83	69.91
	H⁺(ac)	0	0	0
	OH [_] (ac)	-157.293	-229.994	-10.75

 $\Delta G^{0} = \Delta G^{0}(OH^{-}) + \Delta G^{0}(H^{+}) - \Delta G^{0}(H_{2}O) = 79.885 \text{ kJ/mol}$

 $K_w = e^{\{-\Delta G/RT\}} = e^{-32.225} = 1.01 \times 10^{-14}$

 $\Delta H^0 = -229.994 + 0 + 285.83 = 55.836 \text{ kJ/mol}$ Dissociation reaction is endothermic son K_w must increase with T



Acids and bases

ARRHENIUS THEORY (~1885)

ACID: a substance that generates hydrogen ions, H^{+,} in aqueous solutions.

$$HCl_{(ac)} \xrightarrow{H_2O} Cl^{-}(ac) + H^+(ac)$$

BASE: a substance that generates hydroxide ions, **OH**⁻ in aqueous solutions.

$$NaOH(s) \xrightarrow{H_2O} Na^+(ac) + OH^-(ac)$$

SALT: reaction product between an acid and a base

 $HCl + NaOH \longrightarrow NaCl + H_2O$

$$2HCl + Mg(OH)_2 \longrightarrow MgCl_2 + 2H_2O$$

CRITICISM:

- Isolated H⁺ does not exist only in the hydrated form: hydronium cation
- There are bases with no OH⁻ group
- There are salts that are not neutral

Hydroxide *OH*-



Hydronium H₃O⁺



BRONSTED-LOWRY THEORY (1923)

ACID : A substance that donates hydrogen ions to another substance

BASE: A substance that accepts hydrogen ions



$$HCl_{(aq)} + NH_{3(aq)} \longrightarrow NH_{4(aq)}^{+} + Cl_{(aq)}^{-}$$

acid 1 base 2 acid 2 base 1

Why is Na₂O a base?



LEWIS THEORY

BASE: A substance with pairs of electrons that can be shared with an acid $\ddot{N}H_3$

ACID: A substance with empty orbitals to accept pairs of electrons from a base





Self ionization of water

$$H_2O_{(l)} + H_2O_{(l)} \Leftrightarrow OH^-(ac) + H_3O^+(ac)$$

Acid 1 Base 2 Base 1 Acid 2 ¿ACID OR BASIC

$$2H_2O(l) \Leftrightarrow H_3O^+(ac) + OH^-(ac)$$

AMPHOTERIC OR AMPHIPROTIC

Equilibrium constant: lon product of water

$$K_W = [H_3O^+] \cdot [OH^-]$$

 $\begin{array}{c} \mathbf{Pure \ water \ at \ 25 \ \circ \mathbf{C}} & \left[H_3 O^+ \right] = 10^{-7} M \\ & \left[OH^- \right] = 10^{-7} M \end{array} \end{array} \begin{array}{c} \mathbf{K}_W = 10^{-14} \\ & \left[OH^- \right] = \frac{K_W}{[OH^-]} \\ & \left[OH^- \right] = \frac{K_W}{[H_3 O^+]} \end{array} \end{array}$



pH, pOH and pK

In a solution pH is the negative logarithm (base 10) of the molar concentration of dissolved hydronium ions (H_3O^+) ;

$$pH = -\log[H^+] \qquad pOH = -\log[OH^-] \qquad pK_w = -\log K_w = 14$$
$$H^+ \left| \cdot \left[OH^- \right] = K_w = 10^{-14} \qquad \longrightarrow \qquad pH + pOH = 14$$

At 25°C in pure water:

$$\left[H^{+}\right] = \left[OH^{-}\right] \Longrightarrow \left[H^{+}\right]^{2} = 10^{-14} \Longrightarrow \left[H^{+}\right] = 10^{-7} \Longrightarrow pH = 7 \qquad \text{NEUTRAL}$$

At 25°C in a solution

If:
$$[H^+] > [OH^-] \implies [H^+] > 10^{-7} \implies pH < 7$$
 ACID SOLUTION
If: $[H^+] < [OH^-] \implies [H^+] < 10^{-7} \implies pH > 7$ BASIC SOLUTION



Strength of acids and bases

$$H_2O + AH \longleftrightarrow H_3O^+(ac) + A^+$$

Acid dissociation constant, K_a

$$H_2O + B \longleftrightarrow OH^-(ac) + B^+$$
 Base constant, K_b

$$K_{a}' = \frac{[H_{3}O^{+}][A^{-}]}{[HA][H_{2}O]} ; \quad K_{a} = \frac{[H_{3}O^{+}][A^{-}]}{[HA]}; \quad pK_{a} = -\log K_{a}$$
$$K_{b}' = \frac{[OH^{-}][B^{+}]}{[B][H_{2}O]} ; \quad K_{b} = \frac{[OH^{-}][B^{+}]}{[B]}; \quad pK_{b} = -\log K_{b}$$

The value of the acid or base constant is a quantitative measure of the strength of bases and acids







Strong acids and bases: Strong electrolytes, complete dissociation

 $HCl(ac) + H_2O(l) \longrightarrow Cl^{-}(ac) + H_3O^{+}(ac) \qquad NaOH(ac) \longrightarrow Na^{+}(ac) + OH^{-}(ac)$

 $H_2SO_4(ac) + H_2O(l) \longrightarrow HSO_4^-(ac) + H_3O^+(ac)$

Weak Acids: Weak electrolytes, no complete dissociation.

$$\begin{split} HF(ac) + H_2O(l) \Leftrightarrow F^-(ac) + H_3O^+(ac) \cdots K_a &= 6.8 \times 10^{-4} \\ CH_3COOH(ac) + H_2O(l) \Leftrightarrow CH_3COO^-(ac) + H_3O^+(ac) \dots K_a &= 1.8 \times 10^{-5} \\ H_2CO_3(ac) + H_2O(l) \Leftrightarrow HCO_3^-(ac) + H_3O^+(ac) \dots K_a &= 4.4 \times 10^{-7} \\ HCO_3^-(ac) + H_2O(l) \Leftrightarrow CO_3^{-2-}(ac) + H_3O^+(ac) \dots K_a &= 4.7 \times 10^{-11} \end{split}$$

Weak bases: Weak electrolytes, no complete dissociation $NH_3(ac) + H_2O(l) \Leftrightarrow NH_4^+(ac) + OH^-(ac) \cdots K_b = 1.8 \times 10^{-5}$ $CH_3NH_2 + H_2O(l) \Leftrightarrow CH_3NH_4^+(ac) + OH^-(ac) \cdots K_b = 4.3 \times 10^{-4}$



Example: Calculate pH, pOH, $[H^+]$ and $[OH^-]$ of a nitrous acid solution (HNO_2) 0.036 M. Ka=10^{-3.35} (pKa =3.35)

Exact Solution

 $HNO_{2} + H_{2}O \Leftrightarrow NO_{2}^{-} + H_{3}O^{+}$ $2H_{2}O \Leftrightarrow H_{3}O^{+} + OH^{-}$

• 4 Unknowns:

 $HNO_2, NO_2^-, H_3O^+, OH^-$

• We need 4 equations:

 K_a , K_W , mass and charge balances

$$Ka = \frac{\left[NO_{2}^{-}\right] \cdot \left[H_{3}O^{+}\right]}{\left[HNO_{2}\right]} = 10^{-3.35} \quad ; \quad Mass \, Balance : \quad \left[HNO_{2}\right]_{0} = \left[HNO_{2}\right] + \left[NO_{2}^{-}\right]$$
$$K_{W} = \left[H_{3}O^{+}\left[OH^{-}\right] = 10^{-14} \quad ; \quad Charge \, Balance : \quad \left[H_{3}O^{+}\right] = \left[NO_{2}^{-}\right] + \left[OH^{-}\right]$$

$$\begin{bmatrix} OH^{-} \end{bmatrix} = \frac{10^{-14}}{[H_{3}O^{+}]}; \\ [NO_{2}^{-}] = [HNO_{2}]_{0} - [HNO_{2}]; \end{bmatrix} \begin{bmatrix} H_{3}O^{+} \end{bmatrix} = [NO_{2}^{-}] + [OH^{-}] = [HNO_{2}]_{0} - [HNO_{2}] + \frac{10^{-14}}{[H_{3}O^{+}]} \\ Ka = \frac{[NO_{2}^{-}] \cdot [H_{3}O^{+}]}{[HNO_{2}]} = \frac{[H_{3}O^{+}]^{3} - 10^{-14}[H_{3}O^{+}]}{[HNO_{2}]_{0}[H_{3}O^{+}] - [H_{3}O^{+}]^{2} + 10^{-14}}$$
 ¿How is it solved?



$$Ka = \frac{[NO_{2}^{-}] \cdot [H_{3}O^{+}]}{[HNO_{2}]} = \frac{[H_{3}O^{+}]^{3} - 10^{-14} [H_{3}O^{+}]^{2} + 10^{-14}}{[HNO_{2}]_{0} [H_{3}O^{+}] - [H_{3}O^{+}]^{2} + 10^{-14}}$$

$$a = \frac{x^{3} + bx}{cx - x^{2} + d}; x^{3} - ax^{2} + x(b - ac) + da = 0$$
Simplified approach
HNO_{2} + H_{2}O \Leftrightarrow NO_{2}^{-} + H_{3}O^{+}
Dissoc degree $c_{0}(1 - x)$ $c_{0}x - c_{0}x$
Concentration $c_{0} - y$ y y
 $c_{0}cosr_{0}s_{3}s_{3}s_{3}s_{3}s_{6}c_{6}s_{1}2216E-04}$
 $u_{0}cosr_{9}s_{3}s_{4}s_{6}s_{6}e_{0}s_{1} + 1226E-04}$
 $u_{0}cosr_{9}s_{3}s_{4}s_{6}s_{6}e_{0}s_{1} + 12216E-04}$
 $u_{0}cosr_{9}s_{3}s_{4}s_{6}s_{6}e_{0}s_{1} + 1226E-04$
 $u_{0}cosr_{9}s_{3}s_{4}s_{6}s_{6}e_{0}s_{1} + 1226E-04$
 $u_{0}cosr_{9}s_{1}s_{4}s_{6}s_{6}e_{0}s_{1} + 126E-04$
 $u_{0}cosr_{9}s_{1}s_{2} + Kac_{0}c_{1}s_{2} - Kac_{0}s_{2} = 10^{-3.35}$
 $(c_{0}x)^{2} + Kac_{0}c_{1}s_{2} - Kac_{0}s_{0} = 0;$
 $x = 0.1053$
 $[H_{3}O^{+}] = 3.7929 \cdot 10^{-3}$
 $Ka = \frac{[NO_{2}^{-}] \cdot [H_{3}O^{+}]}{[HNO_{2}]} = \frac{(c_{0}x)^{2}}{c_{0}(1 - x)} \approx c_{0}x^{2} = 10^{-3.35}$
 $x = \sqrt{10^{-3.35}/c_{0}}; x = 0.11139$
 $[H_{3}O^{+}] = 4.01 \cdot 10^{-3}$
 $F = \frac{[NO_{2}^{-}]_{coc}}{[NO_{2}H]_{0}} = \frac{4.01 \cdot 10^{-3}}{0.036} \times 100 = 11\%$

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Polyprotic acids

- □ They can donate more than one hydrogen ion per molecule.
- □ They dissociate in stages.
- Each stage has a single dissociation constant

$$H_{n}A_{(ac)} + H_{2}O_{(l)} \Leftrightarrow H_{n-1}A^{-}_{(ac)} + H_{3}O^{+}(ac)$$

$$K_{a1} = \frac{[H_{n-1}A^{-}] \cdot [H_{3}O^{+}]}{[H_{n}A]}$$

$$H_{n-1}A^{-}_{(ac)} + H_{2}O_{(l)} \Leftrightarrow H_{n-2}A^{2-}_{(ac)} + H_{3}O^{+}(ac)$$

$$K_{a2} = \frac{[H_{n-2}A^{2-}] \cdot [H_{3}O^{+}]}{[H_{n-1}A^{-}]}$$

$$H_{n-2}A^{2-}_{(ac)} + H_{2}O_{(l)} \Leftrightarrow H_{n-3}A^{3-}_{(ac)} + H_{3}O^{+}(ac)$$

$$K_{a3} = \frac{[H_{n-3}A^{3-}] \cdot [H_{3}O^{+}]}{[H_{n-2}A^{2-}]}$$



Phosphoric acid: three ionizable hydrogen atoms

$$H_{3}PO_{4 (ac)} + H_{2}O_{(1)} \iff H_{2}PO_{4^{-}(ac)} + H_{3}O^{+}(ac) \qquad K_{a1} = \frac{[H_{2}PO_{4^{-}}] \cdot [H_{3}O^{+}]}{[H_{3}PO_{4}]} = 7.5 \times 10^{-3}$$
Phosphoric acid
$$H_{2}PO_{4^{-}(ac)} + H_{2}O_{(1)} \iff HPO_{4^{2^{-}}(ac)} + H_{3}O^{+}(ac) \qquad K_{a2} = \frac{[HPO_{4^{-}}] \cdot [H_{3}O^{+}]}{[H_{2}PO_{4^{-}}]} = 6.2 \times 10^{-3}$$
dihydrogen phosphate
$$HPO_{4^{2^{-}}(ac)} + H_{2}O_{(1)} \iff PO_{4^{3^{-}}(ac)} + H_{3}O^{+}(ac) \qquad K_{a3} = \frac{[PO_{4^{-}}] \cdot [H_{3}O^{+}]}{[HPO_{4^{-}}]} = 4.8 \times 10^{-13}$$
Hydrogen phoshate
$$HPO_{4^{-}(ac)} + H_{2}O_{(1)} \iff PO_{4^{3^{-}}(ac)} + H_{3}O^{+}(ac) \qquad K_{a3} = \frac{[PO_{4^{-}}] \cdot [H_{3}O^{+}]}{[HPO_{4^{-}}]} = 4.8 \times 10^{-13}$$

Carbonic acid: two ionizable hydrogen atoms $H_2CO_{3 (ac)} + H_2O_{(1)} \iff HCO_{3^- (ac)} + H_3O^+ (ac) K_{a1} = \frac{[HCO_{3^-}] \cdot [H_3O^+]}{[H_2CO_3]} = 4.2 \times 10^{-7}$ $HCO_{3^- (ac)} + H_2O_{(1)} \iff CO_{3^{2^-} (ac)} + H_3O^+ (ac) \qquad K_{a2} = \frac{[CO_{3^{-2}}] \cdot [H_3O^+]}{[HCO_{3^-}]} = 4.8 \times 10^{-11}$



$$\begin{array}{c} \begin{array}{c} \begin{array}{c} \mbox{Conjugated acids and bases} \\ \mbox{Let us consider acetic acid:} \\ \mbox{CH}_3 COOH(ac) + H_2O \Leftrightarrow CH_3 COO^-(ac) + H_3O^+(ac) \\ \mbox{Acetate anion is the conjugate base} \\ \mbox{CH}_3 COO^-(ac) + H_2O \Leftrightarrow CH_3 COOH(ac) + OH^-(ac) \\ \mbox{Both equations are related} \\ \end{array} \\ \begin{array}{c} \mbox{K}_a \in \frac{[CH_3 COO^-][H_3O^+]}{[CH_3 COOH]} \times \frac{[CH_3 COOH][OH^-]}{[CH_3 COO^-]} = [H_3O^+][OH^-] = K_W \\ \mbox{K}_a \cdot K_b = \frac{[CH_3 COO^-][H_3O^+]}{[CH_3 COOH]} \times \frac{[CH_3 COOH][OH^-]}{[CH_3 COO^-]} = [H_3O^+][OH^-] = K_W \\ \mbox{K}_a = \frac{K_W}{K_b} \\ \mbox{K}_b = \frac{K_W}{K_a} = K_h \\ \mbox{If } K_a = 1.8.10^{-5}, \ \mbox{K}_H = 5.6.10^{-10} \\ \mbox{This low } \ \mbox{K}_H value means that acetate ion is a very weak base} \end{array}$$

The conjugate of a strong acid is a weak base The conjugate of a base acid is a weak acid



Can you calculate the conjugate dissociation constants? **Sodium phosphate**

$$PO_4^{3-}(ac) + H_2O_{(I)} \iff HPO_4^{2-}(ac) + OH^-(ac)$$

Phosphate ion

$$HPO_4^{2-}(ac) + H_2O(I) \iff H_2PO_4^{-}(ac) + OH^{-}(ac)$$

Hydrogen phosphate ion

$$H_2PO_4^-(ac) + H_2O_{(I)} \iff H_3PO_4^-(ac) + H_3O^+(ac)$$

Dihydrogen phosphate ion

Phosphoric acid

$$K_{b1} = \frac{[HPO_4^{2^-}] \cdot [OH^-]}{[PO_4^{3^-}]}$$

$$K_{b2} = \frac{[H_2 P O_4^{-}] \cdot [OH^{-}]}{[HP O_4^{2^{-}}]}$$

$$K_{b3} = \frac{[H_3 P O_4] \cdot [OH^-]}{[H_2 P O_4^-]}$$



Hydrolysis

"A salt is completely dissociated into anions and cations"

$$NaNO_3(s) \longleftrightarrow NaNO_3(ac) \longleftrightarrow Na^+(ac) + NO_3^-(ac)$$

HYDROLYSIS: reaction with water of anions and cations coming from the dissociation of a salt

1.- Salts that produce neutral solutions.



There is no hydrolysis



2.- Salts that yield basic solutions

Those coming from a **strong base** and **a weak acid**.

$$CH_3COONa_{(s)} \longrightarrow CH_3COO^{-}(ac) + Na^{+}(ac)$$

 $CH_{3}COO^{-} + H_{2}O \Leftrightarrow CH_{3}COOH + OH^{-}$ $Na^{+} + H_{2}O \leftarrow NaOH + H^{+}$ Strong base

 $CH_3COO^- + H_2O \Leftrightarrow CH_3COOH + OH^-$

Recalling the acid dissociation of acetic acid

 $CH_3COOH + H_2O \Leftrightarrow CH_3COO^- + H_3O^+$

$$K_a = \frac{[CH_3COO^-] \cdot [H_3O^+]}{[CH_3COOH]}$$

 $K_h = \frac{[COOH] \cdot [OH^-]}{[CH_3 COO^-]}$







Example:

Calculate pH and hydrolysis extent (%) in a 0.15 M solution of sodium acetate $Ka_{(Acetic Ac.)} = 1.8 \cdot 10^{-5}$ $CH_3COONa \xrightarrow{H_2O} CH_3COO^- + Na^+$ $CH_3COO^- + H_2O \Leftrightarrow CH_3COOH + OH^ Kh = \frac{[CH_3COOH] \cdot [OH^-]}{[CH_3COO^-]} = \frac{K_W}{Ka}$ $Na^+ + H_2O \leftarrow NaOH + H_3O^+$ $\frac{x^2}{0.15 - r} = \frac{10^{-14}}{1.8 \cdot 10^{-5}} = 5.55 \cdot 10^{-10}$ $CH_3COO^- + H_2O \Leftrightarrow CH_3COOH + OH^-$ 0.15 Inic 0 0 0.15-x Equ. X X $\implies \frac{x^2}{0.15} = 5.55 \cdot 10^{-10} \implies$ $Kh \downarrow \downarrow \downarrow \Rightarrow 0.15 >>> x \Rightarrow 0.15 - x \approx 0.15$ $[OH^{-}] = 9.12 \cdot 10^{-6} M \implies pOH = 5.04 \implies pH = 14 - 5.04 = 8.96$

 $\% Hydrolysis = \frac{[CH_3COO^-]_0 - [CH_3COO^-]}{[CH_3COO^-]_0} \times 100 = \frac{9.12 \cdot 10^{-6}M}{0.15M} \times 100 = 6.1.10^{-3}\%$



3.- Salts that yield acid solutions

Those coming from a **weak base** and a **strong acid**

$$NH_4Cl_{(s)} \xrightarrow{H_2O} NH_4^+(ac) + Cl^-(ac)$$

$$NH_4^+(ac) + H_2O_{(l)} \Leftrightarrow NH_{3(ac)} + H_3O^+(ac)$$

$$Cl^-(ac) + H_2O_{(l)} \leftarrow HCl_{(l)} + OH^-(ac)$$
Strong acid

$$NH_{4(ac)}^{+} + H_2O_{(l)} \Leftrightarrow NH_{3(ac)} + H_3O^{+}_{(ac)}$$

$$K_h = \frac{[NH_3] \cdot [H_3O^+]}{[NH_4^+]}$$

Recall the basic dissociation of ammonia.

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^ K_b = \frac{[NH_4^+] \cdot [OH^-]}{[NH_3]}$$





4.- Salts in which both the anion and the cation hydrolyze

Those coming from **weak acids** and **weak bases**

 $CH_3COONH_4 \xrightarrow{H_2O} CH_3COO^- + NH_4^+$

 $CH_3COO^- + H_2O \Leftrightarrow CH_3COOH + OH^-$

 $NH_4^+ + H_2O \Leftrightarrow NH_3 + H_3O^+$

 $CH_3COO^- + NH_4^+ \Leftrightarrow CH_3COOH + NH_3$

 $K_{h} = \frac{[CH_{3}COOH] \cdot [NH_{3}]}{[CH_{3}COO^{-}] \cdot [NH_{4}^{+}]}$

Recalling the basic and acid dissociations of ammonia and acetic acid

$$Ka = \frac{[CH_{3}COO^{-}] \cdot [H_{3}O^{+}]}{[CH_{3}COOH]}$$

$$K_{b} = \frac{[NH_{4}^{+}] \cdot [OH^{-}]}{[NH_{3}]}$$

$$K_{h} = \frac{[CH_{3}COOH][NH_{3}]}{[CH_{3}COO^{-}][NH_{4}^{+}]} \times \frac{[H_{3}O^{+}]}{[H_{3}O^{+}]} \times \frac{[OH^{-}]}{[OH^{-}]}$$

$$K_{h} = \frac{K_{W}}{K_{a} \cdot K_{b}}$$



Buffers

Combination of weak acids or bases with their conjugate salts

pH remains unchanged when small quantities of strong acids or bases are added

 $CH_{3}COOH + H_{2}O \Leftrightarrow CH_{3}COO^{-} + H_{3}O^{+} \qquad CH_{3}COONa \longrightarrow CH_{3}COO^{-} + Na^{+}$ $[CH_{3}COOH]_{0} \qquad \text{Mix similar molar quantities} \qquad [CH_{3}COONa]_{0}$ $CH_{3}COOH + H_{2}O \Leftrightarrow CH_{3}COO^{-} + H_{3}O^{+}$

Acid dissociates against a preexisting conjugate base \rightarrow Conjugate base hydrolyze against a preexisting acid \leftarrow

This effect is known as common ion effect. At equilibrium

 $[CH_{3}COOH]_{eq} \approx [CH_{3}COOH]_{0} \qquad [CH_{3}COO^{-}] \approx [CH_{3}COO^{-}]_{0}$

 $Ka = \frac{[CH_{3}COO^{-}] \cdot [H_{3}O^{+}]}{[CH_{3}COOH]}; \qquad [H_{3}O^{+}] = K_{a} \frac{[CH_{3}COOH]_{0}}{[CH_{3}COO^{-}]_{0}}; \qquad pH = pK_{a} - \log \frac{[CH_{3}COOH]_{0}}{[CH_{3}COO^{-}]_{0}};$

If $[CH_3COOH]_0 = [CH_3COO^-]_0$ $pH = pK_a = -\log(1.8 \cdot 10^{-5}) = 4.74$ 34



Acid is added: $CH_3COO^-_{(ac)} + H_3O^+_{(ac)} \leftrightarrow CH_3COOH_{(ac)} + H_2O$

$$\frac{[CH_3COOH]}{[CH_3COO^-] \cdot [H_3O^+]} = \frac{1}{K_a} = \frac{1}{1.8 \cdot 10^{-5}} = 5.56 \cdot 10^4$$

Therefore the reaction is totally displaced to the right

 $[CH_{3}COOH]_{eq} = [CH_{3}COOH]_{0} + [H_{3}O^{+}] \qquad [CH_{3}COO^{-}]_{eq} = [CH_{3}COO^{-}]_{0} - [H_{3}O^{+}]$

$$pH = pK_a - \log \frac{[CH_3COOH]}{[CH_3COO^-]} = pK_a - \log \frac{[CH_3COOH]_0 + [H_3O^+]}{[CH_3COO^-] - [H_3O^+]}$$

But if the initial concentrations of acid and conjugate base are in the order of 0.1 M and the amount of added acid is 100 times less.

$$pH = pK_a - \log \frac{[CH_3COOH]_0 + [H_3O^+]}{[CH_3COO^-] - [H_3O^+]} = pK_a - \log \frac{[CH_3COOH]_0}{[CH_3COO^-]_0}$$

So pH remains unaltered



Base is added: $CH_3COOH_{(ac)} + OH^{-}_{(ac)} \leftrightarrow CH_3COO^{-}_{(ac)} + H_2O$

$$\frac{[CH_3COO^-]}{[CH_3COOH] \cdot [OH^-]} = \frac{[CH_3COO^-] \cdot [H_3O^+]}{[CH_3COOH] \cdot [OH^-] [H_3O^+]} = \frac{K_a}{K_W} = \frac{1.8 \cdot 10^{-5}}{10^{-14}} = 1.8 \cdot 10^9$$

Therefore the reaction is totally displaced to the right

 $[CH_{3}COOH]_{eq} = [CH_{3}COOH]_{0} - [OH^{-}] \qquad [CH_{3}COO^{-}]_{eq} = [CH_{3}COO^{-}]_{0} + [OH^{-}]$

$$pH = pK_a - \log \frac{[CH_3COOH]}{[CH_3COO^-]} = pK_a - \log \frac{[CH_3COOH]_0 - [OH]}{[CH_3COO^-] + [OH^-]}$$

But if the initial concentrations of acid and conjugate base are in the order of 0.1 M and the amount of added base is 100 times less.

$$pH = pK_a - \log \frac{[CH_3COOH]_0 - [OH^-]}{[CH_3COO^-] - [OH^-]} = pK_a - \log \frac{[CH_3COOH]_0}{[CH_3COO^-]_0}$$

So pH remains unaltered

How changes pH of a buffer with dilution?



Example:

Calculate the pH of 1L of a solution formed by acetic acid 1 M and sodium acetate 1M when 0.1 moles of HCl gas are added. Assume constant volume. pKa = 4.74.

$$HCl_{(g)} + H_2O \longrightarrow Cl^{-}(ac) + H_3O^+$$

$$CH_3COO^-(ac) + H_3O^+(ac) \longrightarrow CH_3COOH_{(ac)} + H_2O_{(l)}$$

Inic 1.0 0.1 1.0
Equil 1.0-0.1 0 1.0+0.1

$$pH = 4.74 - \log \frac{1.0 + 0.1}{1.0 - 0.1} = 4.66$$

¿What would be the pH if instead of a buffer you have pure water? $[H_3O^+]=0.1moles/1L=0.1M$ pH=1



Titration

Is one of the most important techniques in analytical chemistry. It is used to determine the amount of acids or bases in a solution.

To an unknown acid solution, of volume V_0 , known quantities of a perfectly known base are added and pH is measured. When the amount of added base equals the amount of unknown acid a sudden change appears. This point is called equivalence point.





Indicators

Instead of measuring pH with an specific device (pH-meter) we can use simple indicators. These are molecules whose color depend on the concentration of H_3O^+ .

An example is Phenol Red. It is a weak acid with a $pK_a = 8$ at 20 °C, that ionizes according to the following scheme



This equilibrium can be abbreviated as $HIn + H_2O \Leftrightarrow H_3O^+ + In^-$

The corresponding equilibrium constant is $K_I = \frac{[H_3O^+] \cdot [In^-]}{[HIn]}; \qquad \frac{[In^-]}{[HIn]} = \frac{K_I}{[H_3O^+]}$

where it can clearly be seen that under acidic conditions, the yellow form predominates changing to red under alkaline conditions. Normally, to observe a change in color, concentration of one form must be at least 10 times greater than the other.



<u>Solubility</u>



http://ocw.uc3m.es/ciencia-e-oin/quimica-de-los-materiales/Material%20de%20clase/ tema-5.-cinetica-quimica-termodinamica-y-equilibrio-iv

$$NaCl_{(solid)} \rightarrow NaCl_{(aqueous)} \iff Na_{(aq)}^{+} + Cl_{(aq)}^{-}$$

Types of solutions

- Diluted solution: [solute] < solubility(s)
- Saturated solution without precipitation: [solute] = solubility(s)
- Saturated solution: [solute] > solubility(s)

It is the maximum amount of a solute that can be dissolved in a solvent at a given temperature

Solubility: grams of solute in 1L saturated solution (g/L)

Molar Solubility: moles of solute in 1L saturated solution (mol/L)

Ionic salts: there are no ionic pairs in solution.

Solid is in equilibrium with ions



Solubility Product (K_S)

Let us assume a saturated solution of a generic salt $A_n B_m$:

$$A_n B_m(s) \Leftrightarrow nA^{m+}(ac) + mB^{n-}(ac)$$

The equilibrium constant will be:
$$K = \frac{[A^{m+}]^n [B^{n+}]^m}{[A_n B_m]}$$

Equilibrium concentrations: solubility

Since activity of solids is 1

$$K_s = [A^{m+}]^n [B^{n+}]^m$$
 \longleftrightarrow Solubility Product



For a solution containing ions:

$$nA^{m+}(ac) + mB^{n-}(ac) \Leftrightarrow A_nB_m(s) \downarrow$$

Precipitation will occur depending on the value of the ion concentration product



Precipitation will occur until the ion concentration product equals the solubility product



Example: Calculate the solubility of AgCl in water in the absence and in the presence of a $6.5 \cdot 10^{-3}$ M solution of AgNO₃. Ks(AgCl) = $1.6 \cdot 10^{-10}$ M(AgCl) = 143.4g/mol

a)
$$AgCl(s) \rightarrow Ag^{+} + Cl^{-} K_{S(AgCl)} = 1,6 \cdot 10^{-10}$$

Init pp. 0 0
Equil pp. -s s s Ks = $[Ag^{+}] \cdot [Cl^{-}] = s \times s \implies s = (Ks)^{1/2}$ = $1.3 \cdot 10^{-5} M$

Solubility (g/L) =
$$1.3 \cdot 10^{-5} mol/L \times \frac{143.4g}{1mol} = 1.9 \cdot 10^{-3} g/L$$

b) $6.5 \cdot 10^{-3}$ M of silver nitrate \rightarrow extra [Ag⁺] = $6.5 \cdot 10^{-3}$ M.

$$AgCl \iff Ag^{+} + Cl^{-} \qquad Ks = [Ag^{+}] \cdot [Cl^{-}] = (s + 6.5 \cdot 10^{-3}) \times s = 1.6 \cdot 10^{-10}$$

Init pp. 6.5.10⁻³ 0
Equil pp. -s s + 6.5 10⁻³ s

$$s^{2} + 6.5 \cdot 10^{-3} s - 1.6 \cdot 10^{-10} = 0$$

$$s = 2.5 \cdot 10^{-8} M$$

Solubility (g/L) =
$$2.5 \cdot 10^{-8} mol/L \times \frac{143.4g}{1mol} = 3.6 \cdot 10^{-6} g/L$$



Bio-connections

Antacids.

Gastric acid is secreted by glands in the mucous membrane that lines de stomach in a rate of 2-3 L/day (average adult). The concentration of HCl is 0.03 M. Overeating or emotional factors may increase acid production. To combate the problem there are two approaches:

Remove excess acid by neutralization: antacids

Decrease production of stomach acid: acid inhibitors

Brand name	Neutralizing agents		
Alka-Seltzer	NaHCO ₃		
Maalox	Mg(OH) ₂ , Al(OH) ₃		
Rolaids	NaAl(OH) ₂ CO ₃		
Tums	CaCO ₃		
$HCl + Mg(OH)_2 \rightarrow MgCl_2 + 2H_2O$			
$HCl + Al(OH)_3 \rightarrow AlCl_3 + 3H_2O$			



Buffering in Human Blood.

Metabolic processes maintain blood pH in a narrow range 7.35 -7.45. Small departures can produce serius illness and even variations of about tenths of unit may produce death.



The buffering system is the carbonic acid/hydrogen carbonate system.

 $HCO_3^- + H_3O^+ \leftrightarrow H_2CO_3 + H_2O$ $H_2CO_3 + OH \leftrightarrow HCO_3^- + H_2O$ $H_2CO_3 + OH \leftrightarrow HCO_3^- + H_2O$ The ratio carbonic /carbonate in blood is approximately 1:10 so this buffer has better ability to interact with acids than with bases.

Carbonic acid is controlled by respiration. Excess H_2CO_3 decomposes in CO_2 and water and is removed from the blood by the lungs.

 $H_2CO_3 \Leftrightarrow CO_2 + H_2O$

Hydrogen carbonate concentration is controlled by kidneys



Oxidation and reduction. Concepts

Electrochemical reactions: Electron transfer

OXIDATION REACTION

When an element or molecule transfers electrons (increases oxidation number) Cu, Fe, H2, Fe²⁺, all of them are oxidized

REDUCTION REACTION

When an element or molecule accepts electrons

(decreases oxidation number) Cu^{2+} , Fe^{3+} , H^+ , Fe^{2+} , all of them are reduced

$$Cu \rightarrow Cu^{2+} + 2e^{-}$$

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

$$H_{2} \rightarrow 2H^{+} + 2e^{-}$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

$$Fe^{2+} + 2e^{-} \rightarrow Fe$$

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$

$$H^{+} + e^{-} \rightarrow \frac{1}{2}H_{2}$$



Oxidation state

<u>In monoatomic species</u>: charge of the atom (Cr³⁺, Zn²⁺, Ag⁺)

<u>In polyatomic species</u>: you need the electron distribution among all the atoms within the molecule. Very difficult. Alternative: to apply a reduced set of arbitrary rules: useful although not exact

- 1. The Oxidation State (OS) of pure elements in any allotropic form is zero.
- 2. Oxygen OS is always -2 except in peroxides such as H2O2 and Na2O2 (-1)
- 3. Hydrogen OS is always +1 except in metallic hydrides where it is -1.
- 4. The OS of the other atoms is selected in such a way that the OS sum equals the net charge of the molecule or ion.

Examples: OS of Cl in hypochlorite anion, ClO⁻, is +1 OS of N in nitrite, NO2⁻, is +3 OS of Cr in dichromate anion, Cr2O7²⁻ is +6



Electrochemical reactions: a chemical reaction is electrochemical if OS of reactants and products changes

Potassium Chromate

Chromium Chloride Oxide

 $2CCl_{4} + K_{2}CrO_{4} \Leftrightarrow 2Cl_{2}CO + CrO_{2}Cl_{2} + 2KCl$

Carbon tetrachloride

Phosgene

Potassium chloride

 $CCI_4 : OS CI = -1; OS C = +4$ $K_2CrO_4: OS K = +1; OS Cr (CrO_4^{2-}) = +6$ $CI_2CO: OS CI = -1; OS C = +4$ $CrO_2CI_2: OS CI = -1; OS Cr (CrO_2^{2-}) = +6$

It is not a REDOX process



REDOX reaction

It is reaction in which a REDUCING AGENT transfers electrons to an OXIDIZING AGENT. Alternatively, an OXIDIZING AGENT accepts electrons from a REDUCING AGENT.

An OXIDIZING AGENT becomes reduced and a REDUCING AGENT becomes oxidized





Example:

Given the following process

 $Mg + 2HCl \rightarrow MgCl_2 + H_2$

- a) Identify the oxidation numbers of the elements that take part in the process.
- b) ¿Who oxidizes? Write the Oxidation half-reaction.
- c) ¿Who reduces? Write the Reduction half-reaction.
- d) ¿Who is the Oxidizing Agent? ¿and the Reducing Agent?

Solutions: a) Reactives: Mg(0), H(+1) Cl(-1). Products: Mg(+2), Cl(-1), H(0)

b) Magnesium oxidizes. Mg \rightarrow Mg²⁺ + 2e⁻

c) Hydrogen reduces. $2H^+ + 2e^- \rightarrow H2$

d) Hydrogen ion is the oxidizing agent and metallic magnesium the reducing agent



Balancing oxidation-reduction reactions

ACID MEDIA

Step 1. Write oxidation and reduction half-reactions in their ionic form.

Step 2. Balance the number of atoms different than O and H in each side of the half-reactions.

Step 3. Balance the number of oxygen atoms adding as many H2O molecules as necessary.

Step 4. Balance the number of hydrogen atoms adding as many H⁺ as necessary.

Step 5. Balance the charge adding e⁻ where necessary.

Step 6. Sum the half-reactions to cancel out the number of e⁻.



Example:

Equation:

$$Fe^{2+} + Cr_2O_7^{2-} \rightarrow Fe^{3+} + Cr^{3+}$$

Oxidation:

Reduction:

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^{-} \times 6$$

 $Cr_2O_7^{2-} + 14H^+ + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O \times 1$

Balanced equation:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

×6



BASIC MEDIA

Step 1. Balance in acid media.

Step 2. Sum as many water ionizations as necessary to eliminate hydrogen ions from equation.



EXAMPLE

Equation:

Oxidation:

Reduction:

$$\begin{array}{c} \overbrace{}^{7+} & \overbrace{}^{4+} \\ MnO_4^- + I^- \rightarrow MnO_2 + I_2 \\ 2I^- \rightarrow I_2 + 2e^- & \times 3 \\ MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \\ MnO_4^- + 4H^+ + 4OH^- + 3e^- \rightarrow MnO_2 + 2H_2O + 4OH^- \\ MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- & \times 2 \end{array}$$

Balanced equation:

 $6I^{-} + 2MnO_{4}^{-} + 4H_{2}O \rightarrow 3I_{2} + 2MnO_{2} + 8OH^{-}$



EXAMPLES WITH ORGANIC COMPOUNDS

 $\begin{array}{ccc} 0 & 0 \\ \mathbf{2HCHO} + \mathbf{O}_{2} \rightarrow \mathbf{2} \begin{array}{c} +2 \\ \mathbf{HCOOH} \\ -2 \end{array} \begin{array}{c} OS \text{ of } C \text{ increases from 0 to } +2 \text{ so it is oxidized} \\ OS \text{ of O decreases from 0 to } -2, \text{ so it is reduced} \end{array}$

 $2CH_3CH_2OH + O_2 \rightarrow 2CH_3COOH -2$ OS of C increases from -2 to 0 so it is oxidized OS of O decreases from 0 to -2, so it is reduced -2

-4/3 0 -2 OS of C decreases from -4/3 to -2 so it is reduced $CH_3COCH_3 + H_2 \rightarrow 2CH_3CH(OH)CH_3 OS$ of H increases from 0 to +1, so it is oxidized +1



Electrochemical cells

PARTS OF A CELL: two half cells

- electrolyte: a solution containing ions
- electrode: <u>Anode</u>: Oxidation

•salt bridge: ionic contact between half cells

- electrolyte: a solution containing ions
- electrode: Cathode: Reduction

TYPES OF CELLS



http://www.innovateus.net/science/what-voltaic-cell

Galvanic Cell:

Spontaneous redox reaction ⇒ produces electrical current Cathode: Polarity + Anode: Polarity -

Electrolytic cell:

Non spontaneous redox reaction ⇒ <u>consumes electrical current</u>. Cathode : Polarity -Anode : Polarity +



Galvanic cells

http://ocw.uc3m.es/ciencia-e-oin/quimica-de-los-materiales/Material %20de%20clase/tema-5.-cinetica-quimica-termodinamica-y-equilibrio-iv

Redox Process: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $\Delta G < 0$ Spontaneous



Oxidation Half-reaction

Reduction Half-reaction



Writing conventions about cells

- **1.** Anode is written at the left.
- 2. Cathode is written at the right.
- 3. The limit between the two half cells is written as a double vertical line (||).
- 4. Ions in aqueous solutions are written at both sides of the double vertical line.
- 5. The limit between two phases is represented as a vertical line.
- 6. Different species in the same solution are separated by a comma.

Zn | Zn²⁺ (ac)(1M) || Cu²⁺(ac) (1M) | Cu



Cell Potential

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $E^0 = 1.10V$ Why 1.10 V?

- In REDOX reactions the containers in which Oxidation and Reduction processes take place (the electrodes) can be physically separated (electrodes).
- We select a reference electrode to which zero potential is arbitrarily assigned.



http://ocw.uc3m.es/ciencia-e-oin/quimica-de-los-materiales/Material%20de%20clase/ tema-5.-cinetica-quimica-termodinamica-y-equilibrio-iv



Let us connect the Zn electrode in standard state (Zn²⁺, 1M) to the SHE

Observation:

The spontaneous reaction is the oxidation of Zn and the reduction of H⁺



 $Zn \rightarrow Zn^{2+}(1M) + 2e^{-} \quad \text{Oxidation}$ $\underline{2H^{+}(1M) + 2e^{-} \rightarrow H_{2}} \quad \text{Reduction}$ $Zn + 2H^{+}(1M) \rightarrow Zn^{2+}(1M) + H_{2}$

The relative potential is 0.76 V



Let us connect the Cu electrode in standard state (Cu²⁺, 1M) to the SHE

Observation:

The spontaneous reaction is the oxidation of H2 and the reduction of Cu^{2+}



 $Cu^{2+}(1M) + 2e^{-} \rightarrow Cu$ Reduction $H_{2}(1atm) \rightarrow 2H^{+}(1M) + 2e^{-}$ Oxidation $Cu^{2+}(1M) + H_{2} \rightarrow Cu + 2H^{+}(1M)$

The relative potential is 0.34 V

But which is the sign: + or -? In this case, e⁻ move from SHE to Cu. In the Zn case, the behavior was the opposite. We need a criterion



<u>We write all the half reactions as reductions</u>. And we order them according to the relative tendency to occur against the SHE. If they occur, positive potential. If the opposite, negative potential

 $Cu^{2+}(1M) + 2e^- \rightarrow Cu$ Great tendency Positive E⁰(Cu²⁺/Cu = +0.34 V potential

 $2H^+(1M) + 2e^- \rightarrow H_2$ Null tendency Zero potential $E^0 = 0V$

$Zn^{2+}(1M) + 2e^{-} \rightarrow Zn$	Tendency to occur the opposite reaction: oxidation	Negative Potential	E ⁰ (Zn ²⁺ /Zn) =-0.7	6 V

Generalization: the more positive the potential is, the more tendency the reduction to occur. The more negative, the more tendency the oxidation.



 $=E^0_{reduction}$

 $E^0 = E^0_{cathode}$

 E^0

How can we calculate cell potentials?

$$Cu^{2+}(1M) + 2e^{-} \rightarrow Cu \qquad E^{0} (Cu^{2+}/Cu) = +0.34 V$$
$$Zn^{2+}(1M) + 2e^{-} \rightarrow Zn \qquad E^{0} (Zn^{2+}/Zn) = -0.76 V$$

We write the two half reactions according to their tendency to occur: Cu electrode will reduce and Zn electrode will oxidize.

The cell potential will be the difference between potential of the reduction half reaction minus the potential of the oxidation half reaction.

oxidation

$$Cu^{2+}(1M) + 2e^{-} \rightarrow Cu$$
$$Zn \rightarrow Zn^{2+}(1M) + 2e^{-}$$

$$E^{0} = E^{0}(Cu^{2+}/Cu) + E^{0}(Zn/Zn^{2+}) =$$

= $E^{0}(Cu^{2+}/Cu) - E^{0}(Zn^{2+}/Zn) =$
= +0.34 - (-0.76) = +1.10 V

- Positive cell potential \rightarrow Spontaneous reaction *Why*?



Table of Standard Electrode Potentials

Reduction Half reaction	$E^{0}(V)$
$F_2(g) + 2e^- \rightarrow 2F(ac)$	+2,87
$MnO_4(ac)+8H^+(ac)+5e^- \rightarrow Mn^{2+}(ac)+4H^2O$	+1,51
$Cr_2O_7^{2-}(ac)+14H^+(ac)+6e^- \rightarrow 2Cr^{3+}(ac)+7H_2O$	+1,33
$Fe^{3+}(ac)+1e^{-} \rightarrow Fe^{2+}(ac)$	+0,77
$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-$	+0,41
$Cu^{2+}(ac)+2e^{-}\rightarrow Cu(s)$	+0,34
$2H^+(ac)+2e^- \rightarrow H_2(g)$	0,00
$Ni^{2+}(ac)+2e^{-} \rightarrow Ni(s)$	-0,25
$Cr^{3+}(ac)+3e^{-} \rightarrow Cr(s)$	-0,74
$Zn^{2+}(ac)+2e^{-} \rightarrow Zn(s)$	-0,76
$Al^{3+}(ac)+3e^{-} \rightarrow Al(s)$	-1,66
$Na^{+}(ac)+1e^{-} \rightarrow Na(s)$	-2,71
$Li^{+}(ac)+1e^{-} \rightarrow Li(s)$	-3,05



Electrode potential and free energy

dG = dH - TdS - SdT = dE + PdV + VdP - TdS - SdTSdT = 0 at constant T; TdS = dqVdP = 0 at constant P dE = dq + dwdG = dw + PdV $dw = dw_{PV} + dw_{PV} = dw_{PV} - PdV$ $dG = dW_{elec}$

The free energy change in an electrochemical cell is the reversible nonexpansion work done over the cell



Electric work done BY the system:

welec = $I \times t \times V$; V = E; $I \times t = q$ welec = qE

The free energy change under standard conditions due to the movement of a single electron is:

$$\Delta G^0 = -welec = -q \cdot E^0$$

If n moles of electrones are moving: $\Delta G^0 = -n \cdot (q \cdot NA) \cdot E^0 \iff \Delta G^0 = -n \cdot F \cdot E^0$ 1F = 96485 C/mol

$$\Delta G^{0} = -nFE^{0} \Delta G^{0} = -RT \ln K \longrightarrow E^{0} = \frac{RT}{nF} \ln K$$

The electrode potential is related with the equilibrium constant of the electrode reaction



Spontaneity criteria



Δ G ⁰	К	ΕO	Spontaneity
Negative	> 1	Positive	Spontaneous
0	= 1	0	In equilibrium
Positive	< 1	Negative	Non spontaneous



Nersnt equation

For a given electrochemical reaction





Example

Consider the following galvanic cell Ni | $Ni^{2+}(x M)$ || $Co^{2+}(y M)$ | Co. Calculate how varies the cell potential as a function of y/x. Is this cell spontaneous? What would be the cell potential at equilibrium? Data: $E^{0}(Co^{2+}/Co) = -0.282 V$; $E^{0}(Ni^{2+}/Ni) = -0.236 V$.

As it is written, the oxidation would occur in the Ni electrode and the reduction in the Co electrode. The overall reaction would be Ni + Co²⁺ \rightarrow Co + Ni²⁺. And the cell potential would be $E^0 = E^0$ red – E^0 ox = -0.282-(-0.236) = -0.046. Therefore, the cell will not work as it is written but in the reverse direction.

The spontaneous reaction would be $Ni^{2+} + Co \rightarrow Ni + Co^{2+}$, with a cell potential of $E^0 = 0.046 V$.

Application of the Nernst equation

$$E = E^{0} - \frac{0.059}{2} \log \frac{[Co^{2+}]}{[Ni^{2+}]} = 0.046 - \frac{0.059}{2} \log \frac{y}{x}$$
$$E(10:1) = 0.046 - \frac{0.059}{2} = 0.0165V$$
$$E(1:10) = 0.046 + \frac{0.059}{2} = 0.105V$$

As Co^{2+} concentration is increased, according to the Le Chatelier principle, the reaction should move to the left; that is what happens since the potential decreases. Even more, at a ratio y/x = 36.25, the cell potential would be zero.

When the reaction is at equilibrium no work can be extracted so the $cel_{69}^{}$ potential is zero.



Electrolytic cells **Redox process:** $Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}$ $\Delta G > 0$ NON spontaneous -> Salt bridge **Battery** Cathode Anode Cu Zn Na CI-Cu² Zn²⁺ Electrolyte > **Electrolyte** SO42-**SO4** CuSO4 ZnSO4 soluti Zn Cu n Zn2+ Cu²⁺ $Zn^{2+} + 2e^{-} \rightarrow Zn$ $Cu - 2e^{-} \rightarrow Cu^{2+}$

Reduction

Oxidation



Faraday's Law



http://commons.wikimedia.org/ wiki/File:Michael-faraday3.jpg? uselang=es

- 1. The mass of a substance deposited at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode.
- If "n" electrons participate in a given reaction then "96500.n" Coulombs are needed to deposit 1 mol of product.

$$1 \ mol \ e^- \Leftrightarrow N_A \times q_{e^-} = 6.023 \cdot 10^{23} mol^{-1} \times 1.602 \cdot 10^{-19} C \approx 96500 \ C/mol$$

$$\boxed{1 \ Faraday \ (F) = 96485 \ C/mol}$$

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad 2 \ mol \ e^- \Rightarrow 1 \ mol \ Zn$$

$$Al^{3+} + 3e^- \rightarrow Al \qquad 3 \ mol \ e^- \Rightarrow 1 \ mol \ Al$$

¿How much electrical charge must circulate to reduce a mass "m" of a metal with oxidation number "n" and atomic mass "M"?

$$\mathbf{Q} = \mathbf{I} \cdot \mathbf{t} = \mathbf{F} \cdot \mathbf{n} \cdot \mathbf{m} / \mathbf{M}$$