# UNIT 1: REACTION KINETICS

## **REACTION KINETICS & RATE OF REACTION**

- **reaction rate** = speed at which a reaction occurs
- compare rates of reactants and products using mole ratios
- reaction rate can be measured by:
  - a) mass change open system where gas escapes; use balance & stopwatch
  - b) **colour change** change in intensity; use spectrophotometer & stopwatch
  - c) **pressure change** closed system, with a gas; use pressure gauge & stopwatch
  - d) **temperature change** exothermic, T  $\uparrow$ ; endothermic, T  $\downarrow$ ; use thermometer & stopwatch
  - e) **pH change** acid/base produced; use pH meter & stopwatch
- reaction rate does not remain constant
  - initially fast because [reactants] high
  - $\downarrow$  as rxn proceeds since [reactants]  $\downarrow$



## FACTORS AFFECTING REACTION RATES

- temperature T  $\uparrow$  ,  $\uparrow$  RR
  - for slow rxns,  $10^{\circ}C\uparrow$  doubles RR
- concentration  $\uparrow$  [reactant],  $\uparrow$  RR
- **pressure**  $\uparrow P = \uparrow [], \therefore \uparrow RR$
- nature of reactants due to bonding, reactivity; can not control
- surface area  $\uparrow$  SA,  $\uparrow$  RR (only in reactions with different phases)
- **catalyst**  $\uparrow$  **RR** but is regenerated in original form at end of rxn
- inhibitor  $\downarrow$  RR by combining with catalyst or reactant to prevent rxn
- phase of reactants Aqueous Ions > Gases or Liquids > Solids
- few/weak bonds faster
- fewer particles faster

## **REACTION RATES & COLLISION THEORY**

- not all collisions lead to reaction
- effectiveness of collision depends on:
  - a) geometry must be favourable to allow atoms to rearrange
  - b) **activation energy** = minimum amount of E needed for rxn to occur
- collision theory explains:
  - effect of  $\uparrow$  [ ] closer molecules, more collisions, faster rate
  - effect of  $\uparrow$  T faster molecules, more collisions, faster rate

## ENERGY CHANGES IN CHEMICAL REACTIONS

- **potential energy** = stored energy
  - energy of e- in bonds
  - $\uparrow$  when bonds broken;  $\downarrow$  when new bonds formed
- **kinetic energy** = energy of motion
  - result of movement of molecules
  - can be related to T
- enthalpy (H) = heat of reaction = total KE & PE in system at constant P







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**EXOTHERMIC**  $\rightarrow$  H<sub>products</sub> < H<sub>reactants</sub>  $\rightarrow$   $\Delta$ H is negative

ENDOTHERMIC  $\rightarrow$  H<sub>products</sub> > H<sub>reactants</sub>  $\rightarrow$   $\Delta$ H is positive

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# **UNIT 2: REACTION EQUILIBRIUM**

## **REVERSIBLE REACTIONS**

- = reactions that proceed in the forward  $(R \rightarrow P)$  and reverse  $(P \rightarrow R)$  direction simultaneously
- at beginning, only forward rxn; as rxn proceeds, fwd rxn slows and reverse speeds up; eventually, the system reaches **equilibrium**
- A reversible reaction is said to be at equilibrium when the rate of the forward reaction equals the rate of the reverse reaction.
- characteristics of equilibrium system:
  - system is closed
  - opposite reactions occur at same rate
  - equilibrium was reach starting with either reactants or products
  - T is constant
  - no change in macroscopic properties
  - rate of forward and revers reactions are equal

## PREDICTING SPONTANEOUS REACTIONS

- spontaneous = occurs without outside assistance
- rxns favour side with lower enthalpy  $(\Delta H)$ 
  - exothermic products favoured
  - endothermic reactants favoured
  - exothermic reactions favoured move to minimum enthalpy
- entropy = amount of disorder or randomness
  - rxns favour side with **maximum entropy** ( $\Delta S$ )
  - gases (g) >> solutions (aq) > liquids (l) >> solids (s)
  - look also at moles on each side

## LE CHATELIER'S PRINCIPLE

= when a stress is applied to a system at equilibrium, the system readjusts to relieve or offset the stress and the system reaches a new state of equilibrium

- temperature  $\sqrt{T}$ , shift to side producing heat;  $\uparrow T$  shift away from heat
- concentration  $\uparrow$ [], shift away;  $\downarrow$ [], shift to produce more
- pressure ↑P= ↑[], shift away; ↓P=↓[], shift to produce more
- catalyst speeds up both fwd and rev rxns; reaches EQ faster

## **EQUILIBRIUM EXPRESSIONS & EQUILIBRIUM CONSTANT**

- system at EQ [reactants] and [products] constant; ratio also constant
- equilibrium expression for reaction:  $aA + bB \Rightarrow eE + fF$

$$\begin{split} K_{eq} &> 1 \text{ then products } \text{GREATER THAN reactants} \\ K_{eq} &< 1 \text{ then products } \text{LESS THAN reactants} \\ K_{eq} &= 1 \text{ products } \text{EQUAL reactants} \end{split}$$

Keq =  $\underline{[E]^{e}[F]^{f}}$  = a constant Keq =  $\underline{[products]}$ [A]<sup>a</sup>[B]<sup>b</sup> [reactants]

• solids, pure liquids not included in equilibrium expression (liquid is pure if there is only one)

## DEPENDENCE OF KEQ ON TEMPERATURE

- T is only factor that affects Keq
- · Keq increases when the T of an endothermic reaction is increased
- Keq decreases when the T of an exothermic reaction is increased

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Chemistry 12 Final Review Study Guide EQUILIBRIUM CONSTANT CALCULATIONS (examples) KUSC MOLARITY in ICE TABLES • Suppose that 4.00 moles of HI(g) is placed into a 2.00 L flask at 425°C react to produce H<sub>2</sub> and I<sub>2</sub>. At equilibrium the concentrations of H<sub>2</sub> and I<sub>2</sub> are found to each be 0.214 mol/L. Calculate the value of Keq.  $2HI(g) \neq H_2(g) + I_2(g)$  $\frac{\text{Keq} = [H_2][I_2]}{[HI]^2} = \frac{(0.214)(0.214)}{(1.572)^2}$   $\frac{\text{Keq} = 1.85 \times 10^{-2}}{\text{Keq} = 1.85 \times 10^{-2}}$ I 2.0 2-0.428 +0.214 +0.214 E1.572 0.214 0.214 • A certain amount of  $NO_2(g)$  was placed into a 5.00 L bulb and reacted according to the equation:  $2NO(g) + O_2(g) \neq 2NO_2(g)$ . When equilibrium was reached, the concentration of NO(g) was 0.800 M. If Keq has a value of 24.0, how many moles of  $NO_2$  were originally placed into the bulb?  $= \frac{[NO_2]^2}{[NO_2]} = \frac{[NO_2]}{[NO_2]^2} \frac{[NO_2]}{[NO_2]^2} = \frac{[NO_2]^2}{[(24)(.8)^2(.4))} = \frac{2.48}{100} \frac{M}{100}$ E 0.800 0.400 x-.800 moles NO2=12.4 mo If  $Q = K_{eq}$ , then the system is at EQUILIBRIUM and no shift will occur If Q < K<sub>eq</sub>, then [PRODUCTS] [REACTANTS] is TOO SMALL and shift right, more PRODUCTS • if asked about shift, Trial Keq (Q) is used • Keq = 49 for the equilibrium: If Q >  $K_{eq}$ , then [REACTANTS] is TOO BIG and shift left, more REACTANTS  $2NO(g) + O_2(g) \neq 2NO_2(g)$  If 2.0 mol of NO(g), 0.20 mol of  $O_2(g)$ , and 0.40 mol of  $NO_2(g)$  are put into a 2.0 L bulb, which way will the reaction shift in order to reach equilibrium? \*write Keq first points direction of shift  $Q = [NO_2]^2 = \frac{(0.20)^2}{(1.0)^2(0.1)} = 0.4$ Keq=49 Q = 0.4 Shifts RIGHT to products **UNIT 3: SOLUBILITY EQUILIBRIUM INTRO TO SOLUBILITY** • solution = homogeneous mixtures, uniform throughout • **solute** = substance in lesser [] • solvent = substance in greater [] • electrolyte = substance that dissolves to give electrically conducting solution containing ions • non-electrolyte = substance that dissolves to give non-conducting solution of neutral molecules MOLECULAR SOLUTIONS contain only neutral molecules that are non-electrolytes. IONIC SOLUTIONS contain ions that are electrolytes. • saturated = a solution that has dissolved the maximum amount at a given T saturation exists when: a) some undissolved material is present b) equilibrium exists between the dissolved ions & undissolved solid • solubility = equilibrium concentration of the substance in solution at a given temperature • molar solubility - units of mol/L (M) • saturated solution shown with equilibrium equation of dissolving reaction & crystallization reaction  $Ag_2SO_4(s) \neq 2Ag^+(aq) + SO_4^{2-}(aq)$ 

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## **CALCULATING SOLUBILITY & ION CONCENTRATIONS**

- solubility units mol/L or g/L or g/100mL of solution
- dissociation equation shows the ions formed
- use dilution calculations if mixing solutions

## PREDICTING THE SOLUBILITY OF SALTS

- use solubility table
- low solubility = < 0.1 M to make a saturated solution
- when two ions form a compound having "low solubility" they will form a **precipitate** (ppt)
- compounds with alkali ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Fr<sup>+</sup>), H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, or NO<sub>3</sub><sup>-</sup> are soluble in water
- when adding ions, anions added as sodium salts; cations added as nitrate salts

## WRITING FORMULA, COMPLETE & NET IONIC EQUATIONS

- all ppt reacts used will be double replacement reactions
- formula reaction = balanced chemical reaction with reactants & products given by chemical formula

$$3Ca(NO_3)_2(aq) + 2Na_3PO_4(aq) \approx 6NaNO_3(aq) + Ca_3(PO_4)_2(s)$$

• complete ionic equation = all soluble compounds shown as ions

$$3Ca^{2+} + 6NO_3^{-} + 6Na^{+} + 2PO_4^{3-} = 6Na^{+} + 6NO_3^{-} + Ca_3(PO_4)_2(s)$$

• net ionic equation = spectator ions removed

 $3Ca^{2+} + 2PO_4^{3-} \rightleftharpoons Ca_3(PO_4)_2(s)$ 

## SEPARATING MIXTURES OF IONS BY PRECIPITATION

- qualitative analysis = set of experiments to detect the presence of certain ions in a solution
- using differences in precipitation to separate mixtures of ions

## THE SOLUBILITY PRODUCT & CALCULATIONS

• low solubility substances - very little to make a saturated solution  $\Rightarrow$  reaches a dynamic equilibrium

ex. 
$$PbCl_2(s) \stackrel{\scriptstyle{\Rightarrow}}{\phantom{\Rightarrow}} Pb^{2+}(aq) + 2Cl^{-}(aq)$$

- solubility product expression  $\Rightarrow$  solubility product constant  $\Rightarrow$  Ksp = [Pb<sup>2+</sup>][Cl<sup>-</sup>]<sup>2</sup>
- don't include solids
- see table for Ksp values
- larger Ksp  $\Rightarrow$  products favoured  $\Rightarrow$  greater solubility
- calculating Ksp, molar solubility and concentrations of ions

## PREDICTING WHETHER A PRECIPITATE WILL FORM

• use Trial Ion Product (TIP) and compare to Ksp

TIP >  $K_{sp}$  then **PRECIPITATE** TIP =  $K_{sp}$  then solution is saturated, **NO PRECIPITATE** TIP <  $K_{sp}$  then solution is not saturated, **NO PRECIPITATE** 

When the ion concentrations are less than 0.1 M, the TRIAL ION PRODUCT (T.I.P.) must be calculated to determine whether or not a **PRECIPITATE** will form.

# SOLUBILITY EOUILIBRIA & LE CHATELIER'S PRINCIPLE

- Le Chatelier's Principle = when a stress is applied to a system at equilibrium, the system readjusts to relieve or offset the stress and the system reaches a new state of equilibrium
- common ion effect = decreasing the solubility of a salt by adding another salt with similar ions



[OH<sup>-</sup>] = antilog (- pOH) = 10<sup>-pOH</sup>

at 25°C

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pH + pOH = 14.00

pOH = -log[OH<sup>-</sup>]

ACID & BASE EOUILIBRIUM CONSTANTS • acid ionization reaction of weak acid CH<sub>3</sub>COOH with water:  $K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.76 \times 10^{-5}$  $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^{-}(aq) + H_3O^{+}(aq)$ • base ionization of weak base NH<sub>a</sub>:  $K_{b} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{2}]} = 1.79 \times 10^{-5}$  $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4(aq) + OH^2(aq)$  $K_a \times K_b = K_w$  (at 25 °C,  $K_w = 1.00 \times 10^{-14}$ ) THE RELATIVE STRENGTHS OF ACIDS & BASES • position of equilibrium depends on strength of acids · stronger acids and bases will react to produce their weaker conjugates · weaker acids and bases are favoured in an equilibrium SALT HYDROLYSIS ANIONS (--) hydrolyze to give basic solutions = reaction between water and the cation or anion (or both) contained in the salt to produce an acidic or basic solution CATIONS (+) hydrolyze to give acidic solutions • spectator ions = ions that do not participate in the reaction being considered • spectator cations = alkali metals (group 1) and alkaline earth metals (group 2) • spectator ions = conjugate bases of strong acids: ClO<sub>4</sub>-, I-, Br-, Cl<sup>-</sup> and NO<sub>3</sub>-• metal ions ( $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Al^{3+}$ ) react with water to form acidic solutions • metal oxides - produce basic solutions in water • nonmetal oxides - produce acidic solutions in water (like SO<sub>2</sub> producing H<sub>2</sub>SO<sub>4</sub> in acid rain) • metalloid oxides are amphiprotic  $P \frac{\chi^2}{0.75} = 1.8 \times 10^{-5}$  $\chi = \sqrt{(1.8 \times 10^{-5})}$  $\chi = 3.67 \times 10^{-3}M$  $PH = -\log(3.67 \times 10^{-3})$ CALCULATIONS INVOLVING KA • use ICE tables • Calculate the pH of a 0.75 M acetic acid solution  $(HC_2H_3O_2)$ .  $HC_{2}H_{3}O_{2} + H_{2}O = C_{2}H_{2}O_{3}^{-} + H_{3}O_{3}^{+}$ I 0,75 C - ~ assume! E 0,75-~ ~0,75 I  $\overline{c}$ Ka = [C2H302][H30+] = 1.8×10 DH=2.43 CHC2H2O27 • What mass of NH₄Cl will produce 1.50 L of a solution having a pH of 4.75?  $Ka = [NH3][H30+] \\ [NH4+] \\ 5.6 \times 10^{12} (1.78 \times 10^{-5})$  $NH_4CI \rightarrow NH_4^+ + Q$ PH=4.75 [H30+]=10-4.75 [H304]=1.78×105 NH4++H20 = NH3+ H30 1 → + T X C -1,78×10-5 1.78×105 1.78×10-5 E X-1.78×10-5 1= 0.5651 g= (0, 565mol) (1.54) (53,59 CALCULATIONS INVOLVING KB 01 • Calculate the pH of a 0.10 M NaCN. Nacn->Na++cn-Kb= [HCNJEOH=]  $CN - + H_2O \rightarrow HCN + OH$ [CN-] V=1.43×10-3= EOH I 0.10 2.04×10-5=x2 0.10  $+\infty$ 

• use concentrations of strong acids and bases to find [H<sub>2</sub>O<sup>+</sup>] and [OH<sup>-</sup>]

 $c - \chi$ 

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assume

$$\frac{KW}{KQ(HQN)} = \frac{1 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5}$$

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**MIXING STRONG ACIDS & BASES** 

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## **ACID-BASE TITRATIONS**

- **titration** = quantitative chemical analysis used to determine the unknown concentration of a known reactant
- **equivalence point** = mole ratio in the reaction exactly equals the mole ratio required by the stoichiometry of the reaction

## INDICATORS

- indicator = weak organic acid or base that has different colours for conjugate acid and base forms
- An indicator will be in its conjugate acid (HIn) form in highly acidic solutions.
- An indicator will be in its conjugate base (In-) form in highly basic solutions.
- **transition point** = indicator is mid-way through its colour change and [HIn] = [In-]
- mixtures of indicators blend their colours

At the transition point of any indicator, the following relationships exist:		
[Hin] = [in <sup>-</sup> ]	$\mathbf{K}_{\mathrm{in}} = [\mathbf{H}_{3}\mathbf{O}^{\dagger}]$	pK <sub>in</sub> = pH

## TITRATION CURVES

- **standard solution** = solution with precisely known concentration
- STRONG ACID with a STRONG BASE:



- pH rise almost vertical
- produces neutral solution
- pH=7 at equivalence point
- WEAK ACID with a STRONG BASE:



- initial ↑ in pH
- produces basic solution
- pH>7 at equivalence point
- WEAK BASE with a STRONG ACID:



- initial  $\downarrow$  in pH
- produces acidic solution
- pH<7

#### **BUFFER SOLUTIONS**

- **buffer** = resists large changes in pH resulting from addition of acids or bases
- made of weak acid and salt of its conjugate base or weak base and salt of its conjugate acid
- buffers do not maintain a constant pH, the simply resist large changes

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## PREDICTING SPONTANEOUS REACTIONS

• spontaneous reactions will occur when there is an **oxidizing agent** and a **reducing agent** and the oxidizing agent must be **above** the reducing agent in the table

## **BALANCING HALF REACTIONS**

- must be balanced for mass and charge
  - balance major atoms other than oxygen and hydrogen
  - balance oxygen by adding water  $(H_2O)$
  - balance hydrogens by adding H<sup>+</sup>
  - if basic add OH<sup>-</sup> to both sides to neutralize H<sup>+</sup>
  - balance charge by adding electrons

#### **BALANCING REDOX REACTIONS**

- balance both half-reactions then add together (make sure electrons cancel out)
- balanced redox equations **do not show electrons** and the number of atoms and the total charge are balanced on both sides of the equation
- disproportionation = same chemical undergoes oxidation and reduction
- can balance increase and decrease in oxidation numbers; do not add electrons in this case

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## **REDOX TITRATIONS**

- for determining the concentration of unknown oxidizing or reducing agent
- acidic KMnO<sub>4</sub> is common oxidizing agent for redox titrations
- NaI or KI common reducing agent for redox titrations; two step process that uses starch as an indicator

## ELECTROCHEMICAL CELLS



- **electrochemical cell** = spontaneous redox reaction that produces useful electrical work
- also known as galvanic or voltaic cell
- must be in two separate containers (cells)
- **anode** = electrode where **oxidation** occurs
- **cathode** = electrode where **reduction** occurs

Electrons flow through the wire from the anode to the cathode. The salt bridge keeps the two compartments electrically neutral by allowing ions to migrate between the cells.

- positive cations are attracted to the cathode via salt bridge
- negative anions are attracted to the anode via salt bridge

The electrochemical cell potential is determined by adding the half-cell voltages for the reduction potential and oxidation potential.

- **voltage** = work done per electron transferred = electric potential
- E° = standard reduction potential = voltage at standard state
- oxidation potential = negative of reduction potential
- if E° is **positive**, the reaction is **spontaneous**
- if E° is negative, the reaction is non-spontaneous
- surface area of an electrode does not affect its voltage
- when an electrochemical cell reaches equilibrium, the voltage of the cell is 0.00 V

## **SELECTING PREFERRED REACTIONS**

- when a cell consists of a mixture of substances
- strongest oxidizing agent will become reduced
- strongest reducing agent will become oxidized

## **CORROSION OF METALS**

- corrosion = oxidation of a metal
- rust is just Fe<sub>2</sub>O<sub>3</sub>•xH<sub>2</sub>O
- preventing corrosion
  - isolate from environment
    - protective layer paint, grease, plastic



- electrochemical methods
- **cathodic protection** = protecting a substance from unwanted oxidation by connecting it to a stronger reducing agent

ex. Mg and Zn are stronger reducing agents and become oxidized first = **sacrificial anode** Fe becomes the cathode

- change the conditions
- remove oxygen or increase [OH<sup>-</sup>] ions





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## ELECTROLYSIS

- **electrolysis** = process of supplying electrical energy to a molten ionic compound or a solution containing ions so as to produce a chemical change
- involve non-spontaneous reactions
- require energy to occur = **endothermic**

## **ELECTROLYSIS OF MOLTEN BINARY SALTS**

- contain only two ions
- no salt bridge
- anode connected to + of power source
- cathode connected to of power source
- E° is negative  $\Rightarrow$  must add voltage via power supply





## **ELECTROLYSIS OF AQUEOUS SOLUTIONS**

- ions from salt plus water
- water may behave as an oxidizing or reducing agent
- strongest oxidizing agent becomes reduced (lowest)
- strongest reducing agent becomes oxidized (highest)
- half-cell **overpotential** = difference between actual potential required for electrolysis and calculated potential
- variance is very big for oxidation and reduction of water
- use arrow-head to account for overpotential effect of water

## ELECTROPLATING

- **electroplating** = electrolytic process in which a metal is reduced or "plated out" onto an object connected to the cathode
- **cathode** = material receiving the plating
- electroplating solution = contains ions of metal which is to be plated
- **anode** = same metal which is to be "plated out"





## ELECTROREFINING

- **electrorefining** = process of purifying a metal by electrolysis
- "plating out" a metal from an impure anode onto a pure cathode