

## ORBITALS AND ELECTRONS

Quantum numbers descriptions

Quantum number	Description	Possible values
Principal quantum number (n)	energy level	n=1, 2, 3....
Angular momentum quantum number (l)	orbital shape (s, p, d, f)	l = 0, to ...n-1
Magnetic quantum number (m)	orbital orientation (p <sub>x</sub> , p <sub>y</sub> , p <sub>z</sub> )	m = -l to +l
Spin quantum number (m <sub>s</sub> )	describes spin of electron	m <sub>s</sub> = + ½ or - ½

Each electron has a unique set of quantum numbers.

## ELECTRONIC CONFIGURATION

Electron configuration: describes the location of all of the electrons in an element. e.g. Carbon = 1s<sup>2</sup>2s<sup>2</sup>2p<sup>2</sup>

**Heisenberg Uncertainty Principle:** the position and momentum of a particle cannot both be exactly known at the same time.  
**Pauli exclusion principle:** no two electrons in an atom can have the same set of four quantum numbers (n, l, m, m<sub>s</sub>) which means that each orbital with quantum numbers (n, l, m) can hold at most two electrons with opposite spins.

**Hund's rule:** when electrons added to orbitals of equal energy, a single electron enters each orbital before a second electron with opposite spin enters any orbital. The spins remain parallel if possible. e.g.  
 Nitrogen  
 N = 

↑↓	↑↓	↑↑
↑		
1s	2s	2p <sub>x</sub> 2p <sub>y</sub>
2p <sub>z</sub>		

**Aufbau Principle:** dictates the order in which orbitals fill. *Some exceptions occur in the transition elements.*

1s  
 2s 2p  
 3s 3p 3d  
 4s 4p 4d 4f  
 5s 5p 5d 5f  
 6s 6p 6d 6f

## THE GAS PHASE

### UNITS OF PRESSURE:

1atm = 760 mmHg = 760 torr = 101.325 kPa = 1.01325 barr

### IDEAL GAS POSTULATES

1. molecules are very small compared to the distance b/w them
2. molecules are continuously moving
3. pressure of the gas – collisions of the molecules with container walls
4. molecules do not experience intermolecular forces
5. KE<sub>ave</sub> ∝ T

$$\text{Ideal-gas law: } PV = nRT$$

$$\text{Combined gas law: } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{Charles' law: } \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad P = \text{const}$$

$$\text{Boyle's law: } P_1 V_1 = P_2 V_2 \quad T = \text{const}$$

$$\text{No ones' Law: } \frac{P_1}{T_1} = \frac{P_2}{T_2} \quad V = \text{const}$$

STP – standard temperature (0°C or 273.15 K) and pressure (1 atm)

1 mol of ideal gas occupies V = 22.4 L

*standard conditions* - 25°C and 1 atm

**Dalton's law of partial pressure (mixture of the gases)**

$$P = p_A + p_B + \dots + p_N$$

$$P_A = \chi_A \cdot P$$

$$\chi_A = \frac{n_A}{n_{\text{total}}} = \frac{N_A}{N_{\text{total}}}$$

### GRAHAM'S LAW OF EFFUSION

$$\frac{V_A}{V_B} = \sqrt{\frac{m_B}{m_A}} \quad KE_A = \frac{1}{2} m_A v_A^2$$

$$KE_A = KE_B \text{ at } T_A = T_B \text{ b/c } KE \propto T, \text{ but}$$

$$V_A \neq V_B \text{ at } T_A = T_B$$

*What leads to the gas "ideality":* high T & low P & lower molecular weight or small size of gas molecules

**Real gases:**

- have intermolecular attractions (non-elastic collisions) called Van der Waals forces
- contain molecules that have volume (or measurable size)

$$\left( P_{\text{real}} + a \frac{n^2}{V^2} \right) \cdot (V_{\text{real}} - nb) = nRT$$

## INTERMOLECULAR FORCES

### DISPERSION FORCES:

Describe the attraction between the negatively charged electron cloud of one molecule and the positively charged nuclei of neighbouring molecules

### DIPOLAR FORCES:

Describe the attraction between the negatively charged end of a polar molecule and the positively charged ends of neighbouring polar molecules

### HYDROGEN BONDING:

Involves lone pairs of electrons on an electronegative atom of one molecule and a polar bond to hydrogen in another molecule, they are confined to molecules that contain O, N, and F atoms.

### POLARIZABILITY:

The ease with which the electron clouds are distorted

### MOLECULAR SOLID:

Molecules in molecular solids are held in place by the types of forces: dispersion forces, dipolar interactions, and/or hydrogen bonds

### METALLIC SOLID:

Atoms in metallic solids are held in place by delocalised bonding

### NETWORK SOLID:

Contains an array of covalent bonds linking every atom to its neighbours

### IONIC SOLID:

Contains cations and anions, attracted to one another by coulombic interactions

## SOLUTIONS

molarity (M)	moles of solute/volume of solution. M=n/V
molality (m)	moles of solute/kg of solvent
mole fraction (χ)	moles of solute/total moles
mass percent	mass of solute x 100/ total mass of solution
parts per million (ppm)	mass of solute x 10 <sup>6</sup> /total mass of solution

### Raoult's Law (distillation)

$$P_A = X_A P_A^o$$

Where P<sub>A</sub> = partial pressure of A in solution

X<sub>A</sub> = mole fraction of A in the liquid

P<sub>A</sub><sup>o</sup> = vapour pressure of pure A

### Colligative properties (melting/boiling points etc)

Freezing point depression: salt on the sidewalk in winter lowers the freezing point of H<sub>2</sub>O to prevent the water from freezing

$$\Delta T_f = k_f mi$$

Boiling point elevation: salt in pasta water increases the boiling point of H<sub>2</sub>O so that the water boils hotter (and your pasta cooks more quickly).

$$\Delta T_b = k_b mi$$

Osmotic pressure: increase in pressure due to a solvent crossing a membrane into a more concentrated solution

$$\Pi V = nRT$$



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## ACID-BASE EQUILIBRIA

### ARRHENIUS ACID:

Anything that produces hydrogen ions in aqueous solution

### Arrhenius Base:

Anything that produces hydroxide ions in aqueous solution

### BRØNSTED-LOWRY ACID:

A species that donates a proton is an acid

### BRØNSTED-LOWRY BASE:

A species that accepts a proton is a base

Amphiprotic Species: a chemical species that can both donate and accept protons

### Lewis Acid:

Anything that accepts a pair of electrons

### Lewis Base:

Anything that donates a pair of electrons

### WATER EQUILIBRIUM CONSTANT ( $K_w$ ):

$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$  (at 298 K)

### STRONG ACIDS:

Acids that donate protons to water molecules quantitatively

### Strong Base:

A substance that generates hydroxide ions quantitatively in aqueous solution.

### PH SCALES:

$$\begin{aligned} pH &= -\log[H_3O^+] \quad pOH = -\log[OH^-] \quad pK_a = -\log K_a \\ pK_b &= -\log K_b \quad pH + pOH = 14.00 \quad K_a K_b = K_w \quad pK_a + pK_b = 14.00 \end{aligned}$$

### WEAK ACID:

Acid that reaches equilibrium when only a small fraction of its molecules transfer protons to water

### WEAK BASE:

Generates hydroxide ions by accepting protons from water but reaches equilibrium when only a fraction of its molecules have done so

### APPLICATIONS OF AQUEOUS EQUILIBRIA:

#### BUFFER SOLUTION:

Contains both a weak acid and its conjugate base as major species in solution,

$$pH = pK_a + \log \left( \frac{[A^-]_{\text{initial}}}{[HA]_{\text{initial}}} \right)$$

#### BUFFER CAPACITY:

The amount of added  $H_3O^+$  or  $OH^-$  the buffer solution can tolerate without exceeding a specified pH range.

## CHEMICAL KINETICS

### REACTION MECHANISM:

The exact molecular pathway that starting materials follow on their way to becoming products

### RATE-DETERMINING STEP:

The slowest elementary step in a mechanism

### FIRST-ORDER RATE LAW:

Rate =  $k[A]$ , where A is a reactant in the overall reaction, this can be converted to

$$\ln \left( \frac{[A]_0}{[A]} \right) = kt$$

### HALF-LIFE ( $T_{1/2}$ ), 1<sup>ST</sup> ORDER:

When half the original concentration has been consumed,

$$[A] = 0.5[A]_0, \quad t_{1/2} = \frac{\ln 2}{k}$$

### SECOND-ORDER RATE EXPRESSION:

Rate =  $k[A]^2$ , this can be converted to

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

### BIMOLECULAR ELEMENTARY REACTION:

$A + B \rightarrow \text{products}$  Elementary rate =  $k[A][B]$

### UNIMOLECULAR ELEMENTARY REACTION:

$C \rightarrow \text{products}$  Elementary rate =  $k[C]$

### FIRST STEP IS RATE-DETERMINING:

The predicted rate law for the overall reaction is the rate expression for that first step

### ACTIVATION ENERGY ( $E_a$ ):

Energy barrier, the minimum energy that must be supplied before the reaction can occur

Activated Complex: the molecular arrangement at the point of highest energy along the energy level diagram

## CHEMICAL EQUILIBRIUM

### EQUILIBRIUM CONSTANT:

$$K_{\text{eq}} = \frac{[D]_e^{d_e} [E]_e^{e_e}}{[A]_e^{a_e} [B]_e^{b_e}}$$

$K_{\text{eq}}$  applied only at equilibrium,  $K_{\text{eq}}$  is independent of initial conditions,  $K_{\text{eq}}$  is related to the stoichiometry.

### PURE LIQUID AND SOLID:

The concentrations of pure liquids or solids are always equal to their standard concentrations, therefore division by standard concentration results in a value of 1

### LARGE $K_{\text{eq}}$ :

Indicates that the reaction goes virtually to completion

### LE CHATELIER'S PRINCIPLE:

When a change is imposed on a system at equilibrium, the system will react in the direction that reduces the amount of change.

### TEMPERATURE:

The only variable that causes a change in the value of  $K_{\text{eq}}$ , an increase in temperature always shifts the equilibrium position in the *endothermic* direction.

## THERMODYNAMICS

### CLOSED SYSTEM:

Exchanges energy but not matter with its surroundings

### ISOLATED SYSTEM:

Exchanges neither matter nor energy with the surroundings

### STATE VARIABLES:

Conditions that must be specified to establish the state of a system, pressure ( $P$ ), volume ( $V$ ), temperature ( $T$ ), and amounts of substances ( $n$ )

### PHYSICAL CHANGE OF STATE:

Some of the state variables changes, but the chemical composition of the system stays the same

### CHEMICAL CHANGE OF STATE:

The amounts of reactants and products change

Chemical Reaction: some bonds break, and new bonds form

### STATE FUNCTION:

A property that depends only on the state of the system

### PATH FUNCTION:

A property that depends on how a change takes place

### Molar Heat Capacity:

The amount of heat needed to raise the temperature of 1 mol of substance by 1 Kelvin (1K)

### WORK ( $w$ ):

Energy used to move an object against an opposing force,  $w = Fd$

### FIRST LAW OF THERMODYNAMICS:

$$\Delta E_{\text{sys}} = q_{\text{sys}} + w_{\text{sys}}$$

### Exothermic Process:

If the chemicals release heat, this heat gain raises the temperature of the surroundings

### ENDOTHERMIC PROCESS:

If the chemicals absorb heat, this heat loss lowers the temperature of the surroundings

$$q_{\text{calorimeter}} = C_{\text{cal}} \Delta T, \quad q = nC_{\text{AT}}$$

### ENTHALPY:

A thermodynamic quantity whose change equals the heat flow at constant pressure,

$$\Delta H = \Delta E + \Delta(PV)$$

### STANDARD ENTHALPY OF FORMATION $\Delta H_f^\circ$ :

Enthalpy change accompanying the formation of one mole of a chemical substance from pure elements in their most stable forms under standard conditions

### HESS' LAW:

The enthalpy change for any overall process is equal to the sum of enthalpy changes for any set of steps that leads from the reactants to the products

### MOLAR HEAT OF SOLUTION:

Measures net energy flow that occurs as substance dissolves

### MOLAR HEAT OF VAPORIZATION:

The heat needed to vaporize one mole of a substance at its normal boiling point

### MOLAR HEAT OF FUSION:

Heat needed to melt one mole of a substance at its normal melting point

### SUBLIMATION:

A phase change in which a solid converts directly to a vapour without passing through the liquid phase,

$$\Delta E_{\text{vap}} = \Delta H_{\text{vap}} - RT_{\text{vap}}$$

### SECOND LAW OF THERMODYNAMICS:

Any spontaneous process increases the disorder of the universe

### ENTROPY:

The state function that provides a quantitative measure of disorder and is symbolized  $S$ ,

$$\Delta S = \frac{q_T}{T}$$

### Entropy Change of the Universe:

Total entropy change,

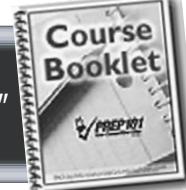
$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

### REACTION ENTROPIES:

$$\Delta S_{\text{reaction}}^\circ = \sum \text{coeff}_p \Delta S^\circ - \sum \text{coeff}_r \Delta S^\circ$$



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## REACTION ENTHALPIES:

$$\Delta H_{\text{reaction}}^{\circ} = \sum \text{coeff}_p \Delta H_f^{\circ} - \sum \text{coeff}_r \Delta H_f^{\circ}$$

## Free Energy (G):

A state function whose change for the system predicts spontaneity and is defined by, Free energy

$$G = H - TS$$

## CHANGE IN FREE ENERGY:

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

$\Delta G_{\text{sys}}$  is negative for all spontaneous processes under conditions of constant temperature and pressure.

## STANDARD MOLAR FREE ENERGY OF FORMATION $\Delta G_f^{\circ}$ :

The change of free energy when one mole of that substance is formed from elements in their standard states,  $\Delta G_f^{\circ} = \sum \text{coeff}_p \Delta G_f^{\circ} - \sum \text{coeff}_r \Delta G_f^{\circ}$

## ENTROPY CHANGE NON-STANDARD CONDITIONS:

Concentrations can be expressed in terms of the standard entropy change and Q:

$$\Delta S_{\text{reaction}} = \Delta S_{\text{reaction}}^{\circ} - R \ln Q,$$

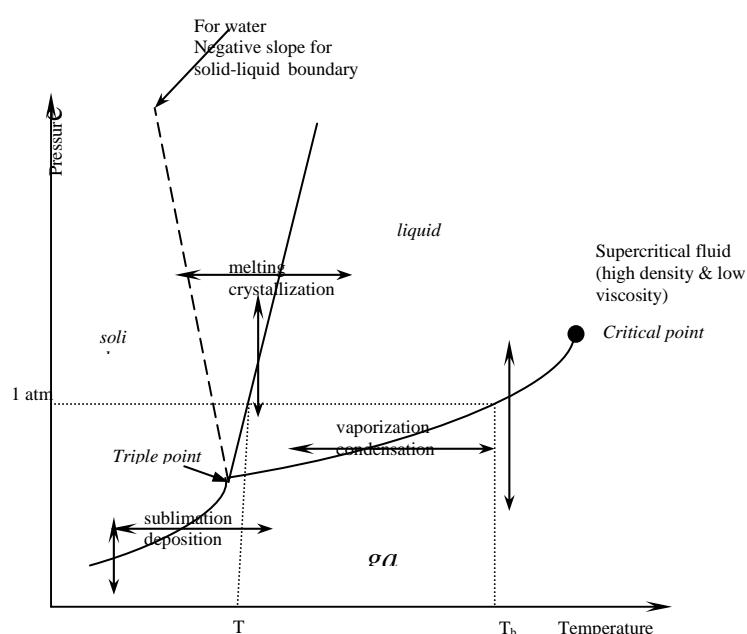
$$\Delta G_{\text{reaction}} = \Delta G_{\text{reaction}}^{\circ} - RT \ln Q$$

## INFLUENCE OF TEMPERATURE ON SPONTANEITY:

$$\Delta G_T^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$\Delta H^{\circ}$	$\Delta S^{\circ}$	$\Delta G^{\circ}$ high T	$\Delta G^{\circ}$ low T	Spontaneity
-	+	-	-	All T
+	-	+	+	No T
+	+	-	+	High T
-	-	+	-	Low T

## Phase Diagram for Water



## ELECTROCHEMISTRY

**Oxidation** – loss of electrons from a substance and an increase in oxidation state

**Reduction** – gain of electrons by a substance and a decrease in oxidation state

**Reducing agent** – a species that loses electrons and is oxidized

**Oxidizing agent** – a species that gains electrons and is reduced

**Anode** – electrode where oxidation occurs, half-reaction with the more negative reduction potential occurs at the anode

**Cathode** – electrode where reduction occurs, half-reaction with the more positive reduction potential occurs at the cathode

## Cell potential:

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

**Gibbs free energy and  $E_{\text{cell}}^{\circ}$ :**

$$\Delta G = -nFE_{\text{cell}}^{\circ}$$

**Relationship between  $E_{\text{cell}}^{\circ}$  and  $K_{\text{eq}}$ :**

$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K_{\text{eq}}$$

**$E_{\text{cell}}$  as a function of concentrations**

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$

**Electrolytic cell** – uses electricity to produce a non-spontaneous reaction

$$\text{number of mol e}^{-} = \text{current} \left( \frac{\text{C}}{\text{s}} \right) \times \text{time(s)} \times \frac{1 \text{ mol e}^{-}}{96,485 \text{ C}}$$



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