

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 _x , p _y , p _z)	m = -l to +l
Spin quantum number (m _s)	describes spin of electron	m _s = + 1/2 or - 1/2

Each electron has a unique set of quantum numbers.

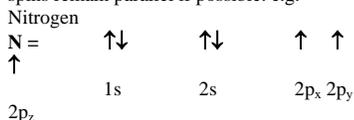
ELECTRONIC CONFIGURATION

Electron configuration: describes the location of all of the electrons in an element. e.g. Carbon = 1s²2s²2p²

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_s) 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.



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 bar

IDEAL GAS POSTULATES

- molecules are very small compared to the distance b/w them
- molecules are continuously moving
- pressure of the gas – collisions of the molecules with container walls
- molecules do not experience intermolecular forces
- $KE_{ave} \propto T$

Ideal-gas law: $PV = nRT$

Combined gas law: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

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

Boyle's law: $P_1V_1 = P_2V_2$ $T = \text{const}$

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

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)

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

$$p_A = \chi_A \cdot P$$

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

GRAHAM'S LAW OF EFFUSION

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

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

$v_A \neq v_B$ 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)

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

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 ⁶ /total mass of solution

Raoult's Law (distillation)

$$P_A = X_A P_A^o$$

Where P_A = partial pressure of A in solution

X_A = mole fraction of A in the liquid

P_A^o = 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 H₂O to prevent the water from freezing

$$\Delta T_f = k_f m_i$$

Boiling point elevation: salt in pasta water increases the boiling point of H₂O so that the water boils hotter (and your pasta cooks more quickly).

$$\Delta T_b = k_b m_i$$

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

$$\Pi V = nRT$$





Need help for exams?

Check out our classroom prep sessions - customized to your exact course - at www.prep101.com

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:

$pH = -\log[H_3O^+]$ $pOH = -\log[OH^-]$ $pK_a = -\log K_a$

$pK_b = -\log K_b$ $pH + pOH = 14.00$ $K_a K_b = K_w$ $pK_a + pK_b = 14.00$

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 ($T_{1/2}$), 1ST ORDER:

When half the original concentration has been consumed,

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

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:

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

K_{eq} applied only at equilibrium, K_{eq} is independent of initial conditions, K_{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_{eq} :

Indicates that the reaction goes virtually to completion

LE CHÂTELIER'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_{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

$$q_{\text{calorimeter}} = C_{\text{cal}} \Delta T, q = nC \Delta T$$

ENTHALPY:

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

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

STANDARD ENTHALPY OF FORMATION ΔH_f° :

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 ,

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

Entropy Change of the Universe:

Total entropy change,

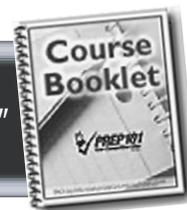
$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

REACTION ENTROPIES:

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



Our Course Booklets - free at prep sessions - are the "Perfect Study Guides."





Need help for exams?

Check out our classroom prep sessions - customized to your exact course - at www.prep101.com

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:

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

ΔG_{sys} is negative for all spontaneous processes under conditions of constant temperature and pressure.

STANDARD MOLAR FREE ENERGY OF FORMATION ΔG_f° :

The change of free energy when one mole of that substance is formed from elements in their standard

$$\text{states, } \Delta G_{\text{reaction}}^{\circ} = \sum \text{coeff}_p \Delta G_f^{\circ} - \sum \text{coeff}_r \Delta G_f^{\circ}$$

ENTROPY CHANGE NON-STANDARD CONDITIONS:

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

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

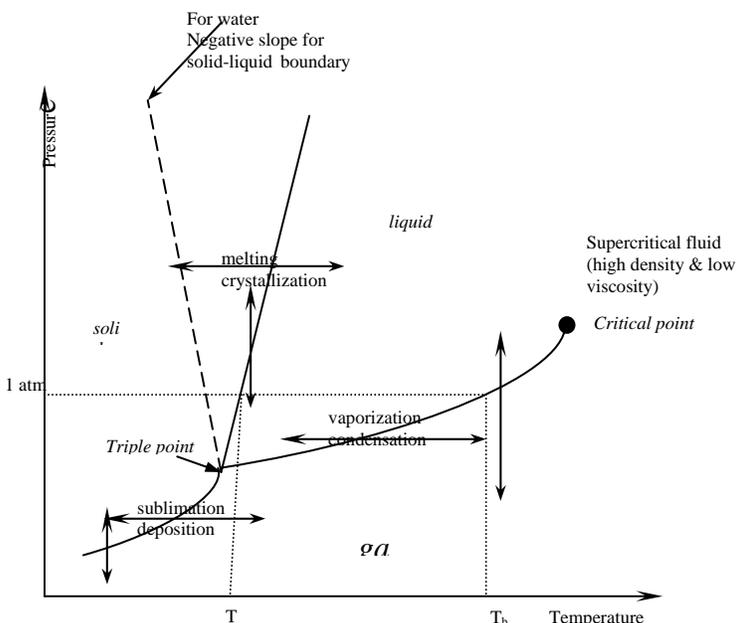
$$\Delta G_{\text{reaction}} = \Delta G_{\text{reaction}}^{\circ} - RT \ln Q$$

INFLUENCE OF TEMPERATURE ON SPONTANEITY:

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

ΔH°	ΔS°	ΔG° high T	ΔH° 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_{cell}° :

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

Relationship between E_{cell} and K_{eq} :

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

E_{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

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



Our Course Booklets - free at prep sessions - are the "Perfect Study Guides."

