Chemistry D-MAVT

Author: joetan

December 21, 2023, Template by Micha Bosshart

1 Basics

1.1 Conversions, Relations and Units

- mass: $[m] = kg$
- volume: $[V] = m^3$
- density: $\rho = \frac{m}{V}$ $[\rho] = \frac{kg}{m^3}$
- ppm: 10^{-6}
- ppb 10^{-9}
- # particles: $[n] = mol$
- molar mass: $[M] = \frac{kg}{mol}$
- molar volume (ideal gas): $V_m ol = 22.41l$
- mass %: $\frac{m_i}{m_{tot}}$
- Avogardo's constant: $N_A = 6.022 \cdot 10^{23}\ \frac{1}{mol}$
- mol fraction: $[\chi] = \frac{mol}{mol}$
- molality: $[M_m] = \frac{mol}{kg}$
- molarity: $[M_c] = \frac{mol}{l}$
- length: $1\ \text{Å} = 10^{-10} m$
- amount of substance: $1mol = 6.022 \cdot 10^{23}$
- kinetic energy: $E_k = \frac{1}{2} mv^2$
- potential energy: $E_p = mg\Delta h$
- electrostatic pot. energy: $E_el = \frac{1}{4\pi\varepsilon_0} \cdot \frac{Q_1 Q_2}{d}$
- spec. heat capacity: $c_s = \frac{q}{m\Delta T}$
- energy of photon: $E = h \cdot \nu = \frac{h \cdot c}{\lambda}$
- Planck's constant: $6.626 \cdot 10^{-34} J \cdot s$
- electron wavelength: $\lambda = \frac{h}{m_e \cdot v}$
- energy: $1eV = 1.60210^{-19} J$ $1cal = 4.18J$
- pressure: $1Pa = 9.87 \cdot 10^{-6} atm$ $= 1.0 \cdot 10^{-5} bar$ $= 7.5 \cdot 10^{-3} torr$
- STP Ideal Gas Law: $0°C = 273.15K, 1bar, 1mol$
- STP Thermodynamics: $25°C = 298.15K, 1bar, 1mol$

1.2 Common Ions

Common Anions

Charge	Formula	Name	Formula	Name
1−	H^-	hydride ion	CH_3COO^- (or $C_2H_3O_2^-$)	**acetate ion**
	F^-	**fluoride ion**	ClO^-	chloate ion
	Cl^-	**chloride ion**	ClO_4^-	**perchlorate ion**
	Br^-	**bromide ion**	NO_3^-	**nitrate ion**
	I^-	**iodide ion**	MnO_4^-	permanganate ion
	CN^-	cyanide ion		
	OH^-	**hydroxide ion**		
2−	O^{2-}	**oxide ion**	CO_3^{2-}	**carbonate ion**
	O_2^{2-}	peroxide ion	CrO_4^{2-}	chromate ion
	S^{2-}	**sulfide ion**	$Cr_2O_7^{2-}$	dichromate ion
			SO_4^{2-}	**sulfate ion**
3−	N^{3-}	nitride ion	PO_4^{3-}	**phosphate ion**

Common Cations

Charge	Formula	Name	Formula	Name
1+	H^+	**hydrogen ion**	NH_4^+	**ammonium ion**
	Li^+	lithium ion	Cu^+	copper(I) or cuprous ion
	Na^+	**sodium ion**		
	K^+	**potassium ion**		
	Cs^+	cesium ion		
	Ag^+	**silver ion**		
2+	Mg^{2+}	**magnesium ion**	Co^{2+}	cobalt(II) or cobaltous ion
	Ca^{2+}	**calcium ion**	Cu^{2+}	**copper(II)** or cupric ion
	Sr^{2+}	strontium ion	Fe^{2+}	**iron(II)** or ferrous ion
	Ba^{2+}	barium ion	Mn^{2+}	manganese(II) or manganous ion
	Zn^{2+}	**zinc ion**	Hg_2^{2+}	mercury(I) or mercurous ion
	Cd^{2+}	cadmium ion	Hg^{2+}	mercury(II) or mercuric ion
			Ni^{2+}	nickel(II) or nickelous ion
			Pb^{2+}	**lead(II)** or plumbous ion
			Sn^{2+}	tin(II) or stannous ion
			Cr^{2+}	chromium(III) or chromic ion
			Fe^{3+}	**iron(III)** or ferric ion
3+	Al^{3+}	**aluminum ion**		

1.3 Trends in Periodic Table of Elements

- Due to "screening", valence electrons only feel effective charge Z_{eff}
- Z_{eff} increases across a row
- Atomic size increases down a column (group) and decreases across row (period)
- Ionic radii: Ions are bigger down column
- Cations are smaller than neutral atom
- Anions are larger than neutral atom
- Ionization energy: Increases across period, decreases down group

Group	Name	Elements
1	Alkali metals	Li, Na, K, Rb, Cs, Fr
2	Alkaline earth metals	Be, Mg, Ca, Sr, Ba, Ra
16	Chalcogens	O, S, Se, Te, Po
17	Halogens	F, Cl, Br, I, At
18	Noble gases	He, Ne, Ar, Kr, Xe, Rn

2 Quantum Mechanics

2.1 Basics

Light

$$\nu = \frac{c}{\lambda}$$

430nm
530nm
630nm

Photon Energy

$$E = h \cdot \nu = h \cdot \frac{c}{\lambda}$$

ν = frequency
c = speed of light
λ = wave length
h = Planck's constant

Rydberg Equation

$$E_H = \frac{hc}{\lambda} = hcR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$R_H = 1.097 \cdot 10^7 m^{-1}$

Orbital Energies

$$E_n = \frac{-hcR_H}{n^2}$$

$$\Delta E = E_{n_f} - E_{n_i} = -hcR_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$\Delta E > 0 (n_f > n_i)$: Photon absorbed
$\Delta E < 0 (n_f < n_i)$: Photon is emitted

Heisenberg's Uncertainty Principle

It is impossible to simultaneously know both the exact momentum of an electron and its exact location in space

$$\Delta x \cdot \Delta(mv) \leq \frac{h}{4\pi}$$

x = position, $mv = p$ = momentum

2.2 Orbitals

Orbital Energies

Quantum Numbers

1. Principial Quantum Number n (1, 2, 3, ...)
2. Angular Quantum Number L : [0, n-1], 0 = s, 1 = p, 2 = d, 3 = f
3. Magnetic quantum Number m_e [−L, L]
4. Spin Magnetic Quantum Number m_s ($-\frac{1}{2}$ or $\frac{1}{2}$)

Pauli Exclusion Principle

No two electrons in an atom can have the same set of four quantum numbers n, L, m_e, m_s

Hund's Rule

When filling degenerate orbitals the lowest energy is attained when the number of electrons having the same spin is maximized

TABLE 6.2 Relationship among Values of n, l, and m_l through $n = 4$

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	
	1	2p	1, 0, −1	3	4
3	0	3s	0	1	
	1	3p	1, 0, −1	3	
	2	3d	2, 1, 0, −1, −2	5	9
4	0	4s	0	1	
	1	4p	1, 0, −1	3	
	2	4d	2, 1, 0, −1, −2	5	
	3	4f	3, 2, 1, 0, −1, −2, −3	7	16

- s-orbital: sphere-like
- p-orbital: dumbbell-like
- d-orbital: usually 4-leafed clover
- f-orbital: 2x2 rounded Rubik's cube/other complicated shapes

3 Chemical Bonds

3.1 Covalent Bonds

- Atoms held together by sharing valence electrons
- Octet Rule: # bonds = 8 - #VE (only strictly applied for groups 1 and 2)
- Exceptions: Hypervalence, less than octet, odd number of VE
- for H and He: # bonds = 2 - #VE
- Bond length: triple < double < single
- Bond strength: triple > double > single

3.2 Polarity and Dipole Moment

$\Delta EN < 0.5$: Even distribution of VE, no dipole moment
$\Delta EN > 0.5$: Polar bond, partial negative charge at atom with higher electronegativity.
$|\vec{\mu}| = Q \cdot r$, $[|\vec{\mu}|]$ = D (Debye), 1D = $3.34 \cdot 10^{-30} C \cdot m$

3.3 Lewis Structure

Drawing Lewis Structures
1. Sum VE of all atoms
2. Write symbols and connect with single bonds
3. Complete octets around non-central atoms
4. Place remaining VE around central atom
5. Try multiple bonds if central atom does not have octet

Alternative Lewis Structure
- More than one Lewis Structure possible
- Calculate formal charges of each atom
- Formal charges closest to zero with negative formal charges on more EN atoms is dominant
- A molecule is most stable when it has the least overall formal charge

Formal Charge = Atom's VE − $\frac{1}{2}$ (Atom's bonding e's) − (Atom's non-bonding e's)

Ex: HCN

1+4+5 = 10

VE	6	4	6
Assigned e's	6	4	6
Formal Charge	0	0	0

VE	6	4	5
Assigned e's	7	4	5
Formal Charge	−1	0	+1

3.4 Ionic Bond

- Ions held together by electrostatic attraction
- Metal loses VE, non-metal gains VE
- Strength quantified by lattice energy
- Bond is considered ionic if $\Delta EN > 2.0$

Some Definitions
Ionization Energy: energy required to ionize (remove) e^- from atom or ion
Electron Affinity: energy change when adding and extra e^- to an atom (typically exothermic)
Lattice Energy: energy required to separate ions in ionic solid to infinite distance

Bookkeeping Systems

Oxidation Number: Charges atoms would have if bonds completely ionic
- Shared e's given completely to more electronegative atom
- Overestimates role of electronegativity

Formal Charge: Charges atoms would have if bonding e's shared equally
- Ignores electronegativity

Partial Charge: Somewhere in between

Oxidation Numbers

Rules: Atoms in elemental form: 0
Monoatomic ions: ionic charge
Nonmetals in ionic/molecular compounds: negative oxidation numbers
Oxygen: −2 (except peroxide ion, O_2^{2-}, −1)
H: +1 (except if bonded to metal, −1)
F: −1 (always)
Cl, Br, I: −1 (except if bonded to oxygen)
Sum of oxidation numbers for atoms in compound equals its net charge

Lattice Energy (e.g NaCl)

$$\Delta H_{lattice} = -\Delta H_f^\circ[NaCl(s)] + \Delta H_f^\circ[Na(g)] + \Delta H_f^\circ[Cl(g)] + I_1[Na] + EA[Cl]$$

3.5 Metallic Bond

- VE shared with entire solid
- Positive core surrounded by negatively charge electron cloud
- Metals have a deficit of VE and therefore do not form covalent bonds
- Freely movable electron cloud is cause for high thermal and electrical conductivity

4 Molecule Models

4.1 VSEPR

1. Draw Lewis structure
2. Count electron domains
3. Determine electron domain geometry
4. Determine molecular geometry from position of atoms

Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry: No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2	Linear	Linear				
3	Trigonal planar	Trigonal planar	Bent			
4	Tetrahedral	Tetrahedral	Trigonal pyramidal	Bent		
5	Trigonal bipyramidal	Trigonal bipyramidal	Sawhorse	T-shaped	Linear	
6	Octahedral	Octahedral	Square pyramidal	Square planar	T-shaped	Linear

5 Aggregate States

5.1 5.1 Intermolecular Forces

1. **Van der Waals Forces (weak)**:
a. **London Dispersion Force**: Instantaneous charge fluctuations leading to repelling and attraction between atoms (always present). Big and long molecules have high dispersion
b. **Dipole-Dipole**: Sum of all dipole moments from polarbonds ⟶ molecular dipole (present in polar molecules)

2. **Hydrogen Bonding (substantial)**:
Occurs between N, O, F atoms and H, which is attracted to unbonded e's of highly EN atoms

3. **Ion-Dipole Interactions**: Dipoles of polar molecules orient themselves with positive and negative ions (present in ionic solid dissolved in polar liquids)

Strength: London Dispersion Force ≈ Dipole-Dipole < H-Bonding < Ion-Dipole

5.2 Liquids

Properites of Liquids
1. **Viscosity**: Resistance to flow. Internal friction of liquid molecules, which slows flow.

2. **Surface Tension**: Energy per unit area of liquid surface. Tendency for liquid surfaces at rest to shrink to the minimal surface area possible.

3. **Vapor Pressure**: Pressure of molecules in gas phase. Dynamics Equilibrium between molecules leaving/entering gas phase, which has to be reestablished when T changes.

Clausius-Clapeyron Equation

$$ln(P) = \frac{-\Delta H_{vap}}{RT} + C$$

$$ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Ex: How much energy is required to heat 1 mol H_2O from −25.0°C to 125°C at 101.3 kPa?

Molar heat capacities:
Ice = 38.1 J mol^{-1} K^{-1}
Liquid water = 75.3 J mol^{-1} K^{-1}
Steam = 37.5 J mol^{-1} K^{-1}

Molar Enthalpies
ΔH_{fus} = 6.01 kJ mol^{-1}
ΔH_{vap} = 40.6 kJ mol^{-1}

Heating Curves

ΔH_{fus} ≡ Heat of fusion
ΔH_{vap} ≡ Heat of vaporization
ΔH_{sub} ≡ Heat of sublimation
$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$
$\Delta H_{vap} > \Delta H_{fus}$

5.3 Solutions and Colligative Properties

Solution: Homogeneous mixture of two ro more substances

solution = solvent + solute(s)

Precipitation Reaction: Reactions that result in the formation of an insoluable product are called precipitation reactions.
e.g. $Ag(NO_3)(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$ $AgCl$ is the solid precipitate

Ionic Equations
1. **Comple Ionic eq.** e.g. $Ag^+(aq) + NO_3^-(aq) + K^+(aq) + Cl^-(aq) \longrightarrow AgCl(s) + K^+(aq) + NO_3^-$ $K^+(aq)$ and $NO_3^-(aq)$ are spectator ions
2. **Net Ionic eq.** e.g. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

(a) Ionic compounds like sodium chloride, NaCl, form ions when they dissolve.
(b) Molecular substances like methanol, CH_3OH, dissolve without forming ions.

Neutralization Reaction
When a solution of an acid and a solution of a base are mixed, a **neutralization reaction** occurs.

$HCl(aq) + NaOH(aq) \longrightarrow H_2O(l) + NaCl(aq)$
(acid) (base) (water) (salt)

$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq)$
$\longrightarrow H_2O(l) + Na^+(aq) + Cl^-(aq)$

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

Concentration

$$\text{Molarity} = \frac{\text{moles solute}}{\text{volume of solution in L}}$$

Thermodynamics of Solutions

1. $(\text{solute})_n \rightleftharpoons n$ solute $\quad \Delta H_{solute}$ (separate solute)
2. $(\text{solvent})_m \rightleftharpoons m$ solvent $\quad \Delta H_{solvent}$ (separate solvent)
3. n solute + m solvent $\rightleftharpoons$ solution $\quad \Delta H_{mix}$ (mix separated solvent and solute)
4. $(\text{solute})_n + (\text{solvent})_m \rightleftharpoons$ solution $\quad \Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix}$

Soluble Ionic Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	CH_3COO^-	None
	Cl^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	Br^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	I^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
Insoluble Ionic Compounds		**Important Exceptions**
Compounds containing	S^{2-}	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}

Gas Solubility

$$S_g = kP_g$$

k: Henry's law constant $[k] = \frac{mol}{m^3 \cdot Pa}$, dependent on solute and solvent
P_g: Gas partial pressure above liquid $[P_g] = Pa$

Colligative Properties
Changes only depend on the amount of solute added and not the type of solute

1. Boiling-Point Elevation

$$\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) = iK_b m$$

m = molality of solute
k_b = molal bp. elevation constant
i = van't Hoff factor ($NaCl \longrightarrow i = 2$)

2. Vapor-Pressure Lowering (Raoult's Law)

$$P_{vap}^{sol} = X_{solvent} \cdot P_{vap}^{pure}$$

P_{vap}^{sol} = vapour pressure of solution
$X_{solvent}$ = mole fraction solvent
P_{vap}^{pure} = vapour pressure of pure solvent

3. Freezing-Point Depression

$$\Delta T_f = T_f(\text{solution}) - T_f(\text{solvent}) = -iK_f m$$

m = molality of solute
k_f = molal fp. depression constant
i = van't Hoff factor

5.4 Osmotic Pressure

The pressure required to counteract osmotic flow of a liquid is called the osmotic pressure. The osmotic flow tries to equalize concentrations across semi-permeable membranes.

$\Pi = i(\frac{n}{V})RT = iMRT$

Π = osmotic pressure
$\frac{n}{V} = M$ = molarity
i = van't Hoff factor

5.5 Ideal Gases

Assumptions for ideal gases:
- Gas particles do not interact
- Gas particles have no volume

1st Gas (Boyle's) Law

$P \cdot V = const.$ if n & T const.

2nd Gas (Charles') Law

$\frac{V}{T} = const.$ if n & P const.

3rd Gas (Avogadro's) Law

$\frac{V}{n} = const.$ if P & T const.

Van der Waals Equations

$(P + \frac{a'n^2}{V^2})(V - nb) = nRT$

a, b are correction factors
$\frac{a'n^2}{V^2}$ corrects interactions at low T.
nb corrects non-negligible volume occupied by molecules at high P

Ideal Gas Law

$P \cdot V = n \cdot R \cdot T$

Molar Gas Volume (STP)

$V_{mol} = 22.41l = 22.41dm^3$

Atmospheric Pressure

$P_{atm} = 760mmHg = 760Torr$
$= 1atm = 101325Pa = 1.01325bar$

Barometer

$P = \rho gh$

Density (IGL)

$\rho = \frac{P}{RT} \cdot M_w$

Molecular Weight (IGL)

$M_w = \frac{\rho RT}{P}$

Partial Pressures Dalton's Law

$P_{tot} = \sum_i P_i$
$P_i = \frac{n_i}{n_{tot}} \cdot P_{tot} = \chi_i \cdot P_{tot}$

Manometer

$P_{gas} = P_{atm} + \rho gh$

$u_{mp} = \sqrt{\frac{2RT}{\mathcal{M}_w}}$

$u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}_w}}$

6 Thermodynamics

6.1 The Three Laws of Thermodynamics

1st Law

Energy can be converted from one form to another, but it is neither created nor destroyed.

2nd Law

The entropy of the universe increases for any spontaneous process.
Reversible Process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$
Irreversible Process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

3rd Law

The entropy of a pure, perfect crystalline substance at absolute zero is zero: $S(0K) = 0$.
There is only one possible microstate.
$S = kln(W) = kln(1) = 0$

6.2 System and Internal Energy

System Types and Internal Energy

Open: Matter and energy can be exchanged with surroundings
Closed: Energy can be exchanged with surroundings (but not matter)
Isolated: Neither matter nor energy is exchanged with surroundings
$\Delta E = E_{final} - E_{initial}$, $\Delta E > 0 \longrightarrow$ system has gained E, $\Delta E < 0 \longrightarrow$ system has lost E.

State functions
- Gibbs free energy, enthalpy, entropy and internal energy are state functions
- Work is not a state function

Internal Energy

$\Delta E = q + w$, q = heat is added to system, w = work done on system
$q > 0$ heat is added to system (endothermic) $w > 0$ work done on system
$q < 0$ heat is lost by system (exothermic) $w < 0$ work done by system

Exothermic Reaction

Calorimetry e.g. H_2O: $c_s = 4.18 \frac{J}{gK}$

Heat capacity = heat required for $\Delta T = 1K$ for specific substance
$q = n \cdot c_m \cdot \Delta T$ c_m = molar heat capacity $[c_m] = \frac{J}{mol \cdot K}$
$q = n \cdot c_s \cdot \Delta T$ c_s = specific heat capacity $[c_s] = \frac{J}{gK}$

Endothermic Reaction

6.3 Enthalpy

Enthalpy

$H = E + PV$ = internal energy + pressure-volume work
$\Delta H = \Delta E + P\Delta V = (q_p + w) - w) = q_p$
Change in enthalpy is equal to heat at constant P
$\longrightarrow$ if ΔV small $\Delta H \approx \Delta E$ $w = -P \cdot V$

$\Delta H_{rxn} = \sum$ enthalpies for bonds broken $- \sum$ enthalpies for bonds formed

Pressure-Volume Work

$W = -P(V_{final} - V_{initial})$

Enthalpies of Reaction (Heat of Reaction)

$\Delta H = H_{final} - H_{initial}$ $\Delta H_{forward} = -\Delta H_{reverse}$
$\Delta H = H_{products} - H_{reactants}$
$\Delta H^\circ_{rxn} = \sum n\Delta H^\circ_f$ (products) $- \sum m\Delta H^\circ_f$ (reactants)

Hess's Law

If a reaction can be written in steps, then enthalpy change of reaction is sum of enthalpy changes for steps.
$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 + ...$

6.4 Entropy

Entropy S

A measure of the tendency for E to spread, which reduces system's ability to do work (related to randomness or disorder in system).
$\Delta S = \frac{q_{rev}}{T}$ q_{rev} = heat flow for reversible process T = absolute temperature
ΔS for phase changes (melting/boiling) isothermal $\longrightarrow q_{rev} = \Delta H_{fus}$ & $q_{rev} = \Delta H_{vap}$

Boltzmann Equation

$S = k_B ln(W)$ W = # microstates $k_B = 1.38 \cdot 10^{-23} \frac{J}{K}$
$\Delta S = k_B ln(W_{final}) - k_B ln(W_{initial}) = k_B ln(\frac{W_{final}}{W_{initial}})$
Entropy increases with the number of microstates of the system.

ΔS for Chemical Reactions

$\Delta S^\circ = \sum nS^\circ$ (products) $- \sum mS^\circ$ (reactants
$\Delta S^\circ = \Delta S^\circ_{sys}$ = standard molar entropies

ΔS_{surr}

$\Delta S_{surr} = \frac{q_{surr}}{T} = \frac{-q_{sys}}{T} = \frac{-\Delta H_{rxn}}{T}$ [at constant P]

6.5 Gibbs Free Energy

Gibbs Free Energy

$G = H - TS$ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- If $\Delta G < 0$, the reaction is spontaneous in the forward direction. (irreversible)
- If $\Delta G = 0$, the reaction is at equilibrium. (reversible)
- If $\Delta G > 0$, the reaction is nonspontaneous in the forward direction (work must be done to make it occur) but the reverse reaction is spontaneous.

Pure Substances

Gibbs Free energy and enthalpy of pure substances are 0

Standard Free Energy of Formation

$\Delta G^\circ = \sum n\Delta G^\circ_f$ (products) $- \sum m\Delta G^\circ_f$ (reactants)

The Importance of T

Example	ΔH	ΔS	$-T\Delta S$	ΔG	Temperature dependence
$2O_3(g) \longrightarrow 3O_2(g)$	−	+	−	−	spontaneous at all T
$3O_2(g) \longrightarrow 2O_3(g)$	+	−	+	+	nonspontaneous at all T
$H_2O(l) \longrightarrow H_2O(s)$	−	−	+	+ or −	spontaneous at low T
$H_2O(s) \longrightarrow H_2O(l)$	+	+	−	+ or −	spontaneous at high T

Spontaneous vs. Nonspontaneous Processes

- If process is spontaneous on one direction $\longrightarrow$ nonspontaneous in reverse
- Nonspontaneous does not mean impossible (add energy)
- Experimental conditions matter
- All spontaneous processes are irreversible (requires work to return to initial state).

Reversible vs. Irreversible Processes

Reversible: Process can be reversed with no change to surroundings. $\Delta S_{univ} = 0$
Irreversible: Surroundings change when process is reversed (e.g. heat transfer)

7 Kinetics

7.1 Reaction Rates

- Convention: Reaction rates are always positive

$Rate = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$

Reaction Order

$Rate = k[A]^m[B]^n$

k : rate constant
m, n: rxn order
$m + n$: overall rxn order

Examples

Overall rxn order	units of k
0	Ms^{-1}
$\frac{1}{2}$	$M^{1/2}s^{-1}$
1	s^{-1}
2	$M^{-1}s^{-1}$
3	$M^{-2}s^{-1}$

7.2 Rate Laws

$[A]_t = -kt + [A]_0$

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

$[A]_t = [A]_0 e^{-kt}$

$ln([A]_t) = -kt + ln([A]_0)$

$t_{1/2} = \frac{0.693}{k}$

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

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

$[A]_t$ = Concentration of A at time t
$[A]_0$ = Concentration of A at time $t = 0$

7.3 Reaction Mechanisms

Arrhenius Equation

$k(T) = \underbrace{(\text{collisions per time})}\cdot\underbrace{(\text{fraction of collisions properly oriented})}\cdot\underbrace{(\text{fraction of molecules with } E > E_a)}$

$k(T) = A \cdot exp[\frac{-E_a}{RT}]$

$ln(\frac{k_1}{k_2}) = \frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1})$

E_a = activation energy
R = universal gas constant
T = absolute Temperature
$[T] = K$

- Approximation:

$ln(k) = \frac{-E_a}{R}\frac{1}{T} + ln(A)$

Increasing temperature by 10°C doubles the rate of reaction.

Reaction Mechanism/ Molecularity

Molecules colliding	Molecularity	Example
one	Unimolecular	$A \longrightarrow Products$
two	Bimolecular	$A + A \longrightarrow Products$
three	Termolecular	$A + A + A \longrightarrow Products$

- Elementary rxns: stoichiometric coefficients = reactions orders/"exponents"

Catalyst: Increases rxn rate but is neither produced nor consumed in overall rxn. Often lowers activation energy

Multistep Reaction

$2A \xrightarrow{k_1} I + C$
$I + B \xrightarrow{k_2} A + D$ } elementary rxns
$A + B \longrightarrow C + D$ overall rxn

$I \equiv$ intermediate

- Assume k1<<k2, step 1 is "rate limiting"

$\Rightarrow$ rate overall $= k_1[A]^2$

8 Acid-Base Chemistry

8.1 Chemical Equilibrium

Law of Mass Action

$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$

Molarity Concentrations
$K_c = \frac{[C]^\gamma[D]^\delta}{[A]^\alpha[B]^\beta}$
$K >> 1$ Equil. on RHS

$K_P = K_c(RT)^{\Delta n}$

Partial Pressures
$K_p = \frac{(P_c)^\gamma(P_D)^\delta}{(P_A)^\alpha(P_B)^\beta}$
$K << 1$ Equil. on LHS

- Δn = change in moles between products and reactants
- $R = 0.08314 \frac{L \cdot bar}{mol \cdot K}$

Reaction Quotient

$Q = \frac{[C]^\gamma[D]^\delta}{[A]^\alpha[B]^\beta}$

- If $Q < K$: forward rxn forms more products
- If $Q > K$: reverse rxn forms more reactants
- For system to come to equilibrium $Q = K$

Types of Equilibria
- Homogeneous equilibria: all substances in same phase
- Heterogeneous equilibria: substances in different phases (exclude pure solids and pure liquids from K)
- For low-solubility ionic solids $K \longrightarrow K_{sp}$ = solubility product

Equilibrium Math
- reverse rxn: $K = K^{-1}_{original}$
- Rxn multiplied with constant factor n: $K = K^n_{original}$
- Multistep rxn: product of K's for individual steps

8.2 Le Châtelier's Principle

Le Châtelier's Principle

If a system at equilibrium is disturbed by a change in concentration, pressure or temperature, the system will shift its equilibrium position so as to counter the effect of the disturbance.

1. Concentration: If a substance is added to a system at equilibrium, the system reacts to consume some of the substance. If a substance is removed from the system, the system reacts to produce more of that substance.
2. Pressure: At constant temperature, reducing the volume of the gaseaous equilibrium mixcture causes the system to shift in the direction that reduces the number of moles of gas.

3. Temperature: When increasing the temperature of a system, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction.

- Catalysed rxns achieve equilibrium faster, but do not change equilibrium constant K.

Equilibria: Connection to Thermodynamics

$\Delta G = \Delta G^\circ + RTln(Q)$ $\Delta G^\circ = -RTln(K)$ $K = exp[\frac{-\Delta G^\circ}{RT}]$
At equilibrium: $\Delta G = 0, Q = K$

ΔG° at STP
ΔG not at STP

8.3 Brönsted Acids and Bases

Acids
Acids are substances that ionize in water to form hydrogen cations (H^+ donors)
e.g.

$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO^-_4(aq)$
$HSO^-_4(aq) \rightleftharpoons H^+(aq) + SO^{2-}_4(aq)$

Bases
Bases are substances that accept hydrogen cations (H^+ acceptors). Bases produce OH^- when dissolved in water.
e.g

$H_2O(l) + NH_3(aq) \rightleftharpoons OH^-(aq) + NH^+_4(aq)$

Autoionization of water (ion-product constant)

$K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0 \cdot 10^{-14}$ (at 25°C)

Common-Ion Effect: Add common ion to manipulate acid-base equilibrium
Buffers: Protect against pH disturbances (comprised of acid and base)

Equilibrium constants

$K_C = K_a = \frac{[A^-][H_3O^+]}{[HA]}$ = acid-dissociation constant
$[HA]$: acid $[A^-]$: conjugate base

$K_C = K_a = \frac{[HB^+][OH^-]}{[B]}$ = base-dissociation constant
$[HB^+]$: conjugate acid $[B]$: base

- **Weak acid**: $K_a << 1$, equilibrium at HA
- **Strong acid**: $K_a >> 1$, equilibrium at A^- (completely ionized, arrow only in forward direction)

8.4 pH-, pOH-, pKa-, pKb- Scales

$pH = -log[H^+] = -log[H_3O^+] = -log[\frac{K_w}{[OH^-]}]$

$pOH = -log[OH^-] == -log[\frac{K_w}{[H_3O^+]}]$

$-log([H^+]) + (-log([OH^-])) = -log(K_w)$

$pH + pOH = 14.00$ (at 25°C)

$pK_a = -log(K_a)$ $pK_b = -log(K_b)$ $pK_a + pK_b = pK_w = 14.00$ (at 25°C)

	Acidic	Neutral	Basic
pH	<7.00	7.00	>7.00
$[H^+](M)$	$>1.0 \times 10^{-7}$	1.0×10^{-7}	$<1.0 \times 10^{-7}$
$[OH^-](M)$	$<1.0 \times 10^{-7}$	1.0×10^{-7}	$>1.0 \times 10^{-7}$

9 Redox Reactions/ Electrochemistry

9.1 General

- Reaction where transfers of electrons occur
- **Oxidation**: Lose an electron, oxidation number is increased (reducing agent is oxidized)
- **Reduction**: Gain an electron, oxidation number is reduced (oxidizing agent is reduced)

9.2 Balancing Redox Reactions

How to balance redox reactions in acidic aqueous solutions

1. Divide reactions into oxidation half-reaction and reduction half-reaction
2. Balance each half-reaction
   - First, balance elements other than H and O
   - Next, balance O atoms by adding H_2O as needed
   - Then, balance H atoms by adding H^+ as needed
   - Finally, balance charge by adding e's as needed
3. Multiply two half-reactions by integers to equate the electrons lost and gained
4. Add half-reactions and, if possible, cancel species appearing on both sides
5. Check to make sure atoms and charges are balanced.

How to balance redox reactions in basic aqueous solutions

1. Balance half-reactions as if they occured in acidic solution (steps 1 and 2)
2. Count number of H^+ in each half-reaction, and add same number of OH^- to each side
   - Why? Neutralizing H^+ with OH^-
   - Equal H^+ and OH^- on same side form H_2O
   - Cancel any H_2O appearing on both sides
3. Multiply two half-reactions by integers to equate the electrons lost and gained
4. Add half-reactions and, if possible, cancel species appearing on both sides
5. Check to make sure atoms and charges are balanced.

9.3 Voltaic Cell/ Battery

Voltaic Cell/ Battery

- **Activity series**: any metal is oxidized by metals below it (spontaneous).
- **Components**:
1. **Electrodes**: solid metals connected to external circuit. Anode loses mass, whilst cathode gains mass (deposition).
2. **Electrolyte**: liquid with ions that can conduct electrical current
3. **Salt bridge**: tube containing electrolyte solution facilitating ion migration

Cell Potentials

$1V = \frac{1.6 \cdot 10^{-19} J}{1.6 \cdot 10^{-19} C}$

Cell Voltage at STP (Thermodynamics)

$E^\circ_{cell} = E^\circ_{red}$ (cathode) E°_{red} (anode)

Gibbs Free Energy

$\Delta G^\circ = -nFE^\circ$ $E^\circ = \frac{\Delta G^\circ}{-nF} = \frac{-RTln(K)}{-nF} = \frac{RT}{nF}ln(K)$

If $E^\circ_{cell} > 0, \Delta G^\circ < 0 \longrightarrow$ rxn is spontaneous

$\Delta G^\circ = J/mol$ of rxn
$F = 96485 \frac{C}{mol}$ = Faraday's constant
n = moles of e's transferred in rxn
K = Equilibrium constant

10 Appendix

- **Intensive Properties**: Do no depend on the system size or the amount of material. (e.g. temperature, refractive index, density, E°_{cell}
- **Extensive Properties**: Depend on system size. (e.g. mass, volume, entropy)

Atoms
- **Atomic Number**: # of protons in atom of particular element
- **Isotopes**: Same element with different # neutrons
- **Mass Number**: # of protons and neutrons
- **Atomic Mass Scale**: $\frac{1}{12}C = 12u$ $m_p = 1.0073u$ $m_n = 1.0087u$ $m_e = 5.486 \cdot 10^{-4}u$ $1u = 1.6605 \cdot 10^{-27}kg$
- **Atomic Weight**: Average atomic mass of all isotopes of an element, weighted by their natural abundance in atomic mass units
- **Atomic Mass**: The mass of an atom's electrons, protons and neutron in atomic mass units

Metathesis and Precipitation Reactions: - **Metathesis**: Two ionic solids dissolve and exchange partners
- If cation/ anion pair is strongly attracted, a solid preciptate is formed.

11 Author's notes

I neither guarantee that the following summary is complete nor absolutely correct. Please forward any corrections or suggestions for improvements to joetan@ethz.ch. This summary was written specifically for Prof. David Norris' Chemistry course. Should you wish to publish an improved version with your own notes and changes, please make clear that it is not the original version.
Viel Erfolg! Glück brucht mer nur wemers nöd chän.