Chemistry - Cheat sheet

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## Solubility Guidelines for Common Ionic Compounds in H_2O

Soluble, Ionic Compounds containing	Important Exceptions
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+} Ag^+ , Hg_2^{2+} , and Pb^{2+}

Insoluble, Ionic Compounds containing	Important Exceptions
S^{2-}	Compounds of NH_4^+ , the alkali metal cations,Ca^{2+} , Sr^{2+} , andBa^{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+} , andBa^{2+}

Gases

Ideal gas law

ideal gas: no intermolecular interactions between particles
STP: 273.15 K, 1 atm = 101.325 kPa

$$PV = nRT = Nk_BT$$

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

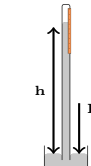Partial pressure $\quad P_i = \frac{n_i}{n_{tot}}P_{tot}$
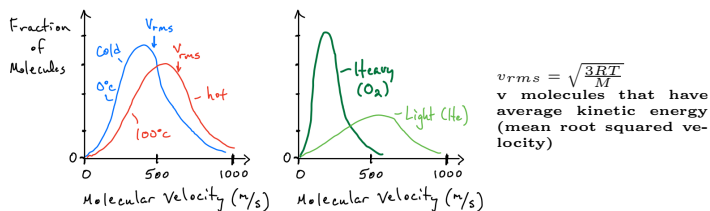
$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

v molecules that have average kinetic energy (mean root squared velocity)

Pressure measurement

Barometer $P = \rho g h$ $\qquad$ Manometer $\quad P_{gas} = P_{atm} + \rho g h$

$P_{atm} = 101.325 kPa = 760 mmHg = 760 torr$

Thermodynamics

Ethalpy H

$$H = E + PV \qquad \Delta H \overset{\dot{P}=0}{=} q_p$$

- $\Delta H > 0 \Rightarrow$ system gained heat
- $\Delta H < 0 \Rightarrow$ system lost heat

state function: only depends on current state(p,V...)/path independent: E, H

Hess's Law

$$\Delta H_{rxn} = \sum_i \Delta H_i$$

$$\Delta H_{rxn}^0 = \sum_{prod,j} b_j \cdot \Delta H_{f,j}^0 - \sum_{react,i} a_i \Delta H_{f,i}^0$$

Bond enthalpy

$$\Delta H_{rxn} = \sum_{i:\text{bonds broken}} \Delta H_i - \sum_{i:\text{bonds formed}} \Delta H_i$$

Reactions

- Spontaneous p. = p. occur w/o assistance
- Reversible = p. can be reversed w/no change to surroundings *infinitisimal* change
- Irreversible = surroundings changed when process is reversed

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- All real p. are irreversible
- All spontaneous p. are real
- All spontaneous p. are Irreversible
- To return system to initial state ⇒ requires work
- While E is conserved during spontaneous p. E tends to spread out and become less usefull

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3rd law of thermodynamics

- Pure, crystalline solid substance at $T = 0K$ has $S = 0$
- For rxn: $\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H_{rxn}^0}{T}$
- $S = ln(W) * k_B$ whereas **W** increases with V,p,N, complexity of molecule
- Reversible p. : $\Delta S_{univ} = 0$ and $\Delta G = 0$
- Irreversible p. : $\Delta S_{univ} > 0$ and $\Delta G > 0$
- Entropy of the universe increases for any spontaneous p

Gibb's free energy

maximum amount of work can extract from
- $G := H - TS$
- at const. $T \Rightarrow \Delta G = \Delta H_{sys} - T\Delta S_{sys}$

ΔH	ΔS	$-T\Delta S$	ΔG	Rxn Characies
-	+	-	-	
+	-	+	+	
-	-	+	+ or -	
+	+	-	+ or -	

Thermodynamics of solution

calorimetry: $\quad \boxed{\Delta H_{rxn} = q_{rxn} = -q_{H_2O}}$

$$\boxed{\Delta Q = c_s * m * \Delta T = c_m * n * \Delta T} \quad \textbf{1 cal = 4.182 J}$$

solvent + solute $\underset{dissolve}{\overset{crystallize}{\rightleftharpoons}}$ solution

$$
\begin{array}{ll}
(solvent)_n \rightarrow n \cdot solvent & \Delta H_{solvent}(separate\ solvent) \quad (1)\\
(solute)_m \rightarrow m \cdot solute & \Delta H_{solute}(separate\ solute) \quad (2)\\
n \cdot solvent + m \cdot solute \rightarrow solution & \Delta H_{mix}(mix\ separate\ solvent\&solute) \quad (3)\\
\hline
(solvent)_n + (solute)_m \rightarrow solution & \Delta H_{soln}(total\ enthalpy\ change)
\end{array}
$$

- $\Delta H_{soln} > 0 \Rightarrow -T\Delta S_{soln}$ musst be sufficient $\Rightarrow$ more likely at high T
- $\Delta H_{soln} < 0$ **typically forms solution for any** $c(solute)$, completly miscible (mixable)

Lattice energy and phase diagram
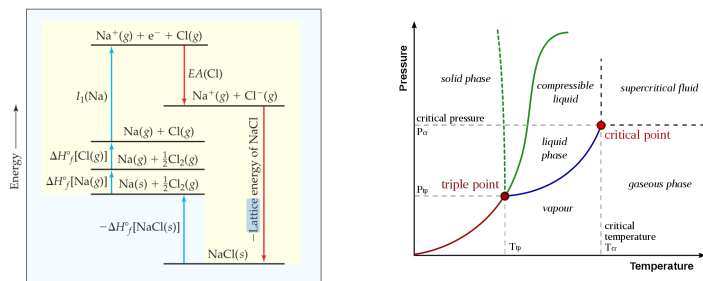
supercritical fluid: no distinction between liquid and gas, no surface tension

Factors affecting solubility

- **strong solute-solvent** interactions favor higher solubility
- substances with similar interactions tend to be soluble in each other
- Temperature
  - Ion solubility in H_2O increases with T $\Rightarrow \Delta S_{soln} > 0$
  - Gas solubility in H_2O decreases with T $\Rightarrow \Delta S_{soln} < 0$
- Pressure $\quad \boxed{S_g = kP_g}$ $\quad S_g$ gas solubility, k Henry's law constant, P_g partial pressure

Colligative Properties

= Solute effects liquid, depends only on amount of solute
ideal solution: solvent-solvent and solute-solvent interaction are the same

- Boiling point elevation $\quad \boxed{\Delta T_{bp} = T_{bp}^{soln} - T_{bp}^{soln} = iK_b m}$, m = molarity of solute, K_b = molal bp elevation constant, i = van't Hoff factor =
$$\begin{cases} 1, & \text{for non-electrolytes} \\ \# \text{ ions produced,} & \text{for electrolytes} \end{cases}$$

- Vapor - pressure lowering Raoult's law: $\quad \boxed{P_{vap}^{soln} = X_{solvent} \cdot P_{vap}^{pure}}$

- Freezing - point depression $\quad \boxed{\Delta T_{fp} = -iK_f m}$

- Osmotic pressure $\quad \boxed{\Pi = iMRT}$ $\quad \Pi$ osmotic pressure to counteract osmotic flow
- hypertonic $\Pi > \Pi_{ref}$ and hypotonic $\Pi < \Pi_{ref}$

Expressions of concentration

x $\quad$ mole fraction $= \frac{n(\text{solute})}{n_{tot}}$ $\qquad$ mass% $= \frac{m(\text{solute})}{m_{tot}}$

c $\quad$ molarity $= \frac{n(\text{solute})}{V_{tot}}$ $\qquad M$ $\qquad$ ppm = mass% $\cdot 10^6$

b $\quad$ molality $= \frac{n(\text{solute})}{m(\text{solvent})}$ $\qquad m = \frac{mol}{kg}$ $\qquad$ ppb = mass% $\cdot 10^9$

Properties of liquids

- viscosity: resitsance to flow, interactions slow flow
- surface tension: Energy unit per area of liquid surface, minimize surface where intermol. interactions are missing

- vapor pressure: pressure of molecules in gas phase (volatile liquid has small E_{int} and high p_v)

Clausius-Clapeyron equation

$$\ln P_{vap} = -\frac{\Delta H_{vap}}{RT} + C$$

Chemical Kinetics

Reaction rate: $|\dot{c}(A)|$ $\quad$ For general rxn: $\alpha A + \beta B \rightarrow \gamma C + \delta D$ Rate $= -\frac{1}{\alpha}\frac{d[A]}{dt} = -\frac{1}{\beta}\frac{d[B]}{dt} = \frac{1}{\gamma}\frac{d[C]}{dt} = \frac{1}{\delta}\frac{d[D]}{dt}$

Rate laws

- general $\quad \boxed{\text{Rate } = k[A]^n[B]^m \cdots}$
- m,n reaction orders
- $m, n \in \{0, \frac{1}{2}, 1, 2, \cdots\}$
- m,n are **not** necessarily equal α, β
- overall reaction order $= m + n + \cdots$
- fast rxns $k > 10^9$ slow rxns $k < 10$

Using rate laws rxn $A \rightarrow B$

- $-\frac{d[A]}{dt} = k[A]^m$
- **First-order** $m = 1$: $\quad \boxed{\ln[A]_t - \ln[A]_0 = -kt}$ $\quad \boxed{t_{1/2} = \frac{\ln 2}{k}}$
- **Second-order** $m = 2$: $\quad \boxed{\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}}$ $\quad \boxed{t_{1/2} = \frac{1}{k[A]_0}}$
- **Zero-order** $m = 0$: $\quad \boxed{[A]_t = -kt + [A]_0}$ $\quad \boxed{t_{1/2} = \frac{[A]_0}{2k}}$

Collision model

Temperature dependence of rate law

- $k(t) =$ (collision per time) $\cdot$ (fraction of collisions properly oriented) $\cdot$ (fraction molecules with $E > E_A$)
- $\boxed{k(t) = A \cdot \exp\frac{-E_A}{RT}}$
- $ln(\frac{k_1}{k_2}) = \frac{E_A}{R}(\frac{1}{T_2} - \frac{1}{T_1})$ for typical E_A, T, rxn rate doubles for $\delta T = +10K$

Elementary reactions

- simple step where 1 'thing' happens, typically 1 bond breaks/forms
- $\boxed{m = \alpha \text{ and } n = \beta \text{ for elementary rxn}}$
- process to determine rxn mechanism
  1. measure rates
  2. propose mechanism
  3. check consistency

Law of mass action

$$K = \frac{k_{forward}}{k_{reverse}} = \frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta} \qquad a_i = \begin{cases} \frac{[i]}{1M} \\ \frac{P_i}{1bar} \end{cases} \qquad \boxed{K_P = K_C(RT)^{\Delta n}}$$

- note: requires closed system
- all rxns are elementary near equilibrium
- K is rxn specific
- K_C & K_P are unitless
- for pure solids/liquids $a = 1$
- for multistep rxn $K = \Pi_i K_i$
- rate-limiting step: **k1 << k2** → rate overall is only dependent on k1

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

- $Q < K$ forward rxn forms more product
- $Q > K$ reverse rxn forms more reactant

Le Chatelier Principle: If a system at equil. is disturbed by change in T, P or c system shifts its equil. to counteract disturbance

endothermic: $A + \Delta E \rightleftharpoons B$ and exothermic: $A \rightleftharpoons \Delta E + B$
V decreases → p increases → reaction is preferred which produces less molecules

Relation to thermodynamics: $\quad \boxed{\Delta G = \Delta G^0 + RT \ln Q}$

At equil.: $\Delta G = 0 \Rightarrow \Delta G^0 = -RT \ln K$

Electronic Structure

- $c = \lambda * f$
- Rydberg Equ: $E_H = \frac{hc}{\lambda_H} = hcR_H(\frac{1}{n_1^2} - \frac{1}{n_2^2})$
- Orbitals
  - principal quantum number, $n \in \{1, ...\}$
  - angular quantum number, $l \in \{1..., n-1\}$

0	1	2	3
s	p	d	f

  - Magnetic quantum number, $m_l \in \{-l, ..., l\}$ (orientation in space)
  - Spin magnetic quantum number, $m_s \in \{-\frac{1}{2}, \frac{1}{2}\}$
  - Ex. Se: $[Ar]3d^{10}4s^24p^4$

Pauli exclusion principle

- Order of subshells ? → use periodic table $s = 2, p = 6, d = 10, f = 14$
- Hunds rule
- Exception: half/filled orbitals are more favourable

Screening

- For given shell(s) v.e. repelled by core e ('screen') $\Rightarrow$ v.e. feel $Z_{eff} < Z$
  Effect stronger for subshells further from nucleus
- Trends

Bonds

Bond polarity
- If electro negativity $\geq 2 \Rightarrow$ ionic bond

Dipol Moments
- $|\vec{\mu}| = Qr$
- pointing from - to +
- very polar bonds $\Rightarrow$ large $|\vec{\mu}|$

Ionic vs covalent
- continuum of behavior
- more covalent $\Rightarrow$ 'molecular behavior' low melting/boiling T
- more ionic $\Rightarrow$ ionic solid brittle high boiling T
- electro negativity difference not perfect: oxidation # of metals increases $\Rightarrow$ bonding more covalent

Molecular geometry
domain: bonding + nonbonding pairs
molecular geometry: just position of atoms

Drawing Lewis Structures
- Octet rule Atoms want 8 v.e.'s
1. sum v.e.'s of all atoms
2. write symbols and connect with single bonds
3. complete octets around non-central atoms
4. place remaining v.e.'s around central atom
5. try multiple bonds if central atom doesn't have octet

Exceptions to the octet rule
- odd # e
- less then octet v.e.'s
- more then octet of v.e.'s

Formel charge
- Formel Charge = v.e.'s - $\frac{1}{2}$ atom's bonding e's - atom's non-bonding e's
- dominent Lewis structure have formel charges closet to 0, and $\ominus$ on more electro negative atoms

Valance-shell electron pair repulsion
1. draw Lewis
2. count e domains
3. determine e domain geometry
4. determine molecular geometry from position of atoms

#	electron domain geometry	molecular geometry	angle	examples
2 $X{-}A{-}X$ AX_2		linear	$180°$	H_2
3 AX_3 AX_2E_1		triangular planar bent	$120°$ $\approx 115°$	NO_3^- SO_2
4 AX_4 AX_3E_1 AX_2E_2		tetrahedral trigonal planar bent	$109.5°$ $\approx 107°$ $\approx 104°$	CH_4 NH_3 H_2O

5	AX_5	trigonal bipyramidal	$90°/120°$	PCl_5
AX_4E_1		seesaw	$\approx 175°/110°$	SF_4
AX_3E_2		T-shape	$\approx 87.5°$	ClF_3
AX_2E_3		linear		XeF_2
6	AX_6	octahedral	$90°$	SF_6
AX_5E_1		square pyramidal	$\approx 85°$	BrF_5
AX_4E_2		square planar	$90°$	XeF_4
7	AX_7	pentagonal bipyramidal	$90°/72°$	IF_7
AX_6E_1		pentagonal pyramidal	$\approx 90°/\approx 72°$	$XeOF_5^-$
AX_5E_2		pentagonal planar	$72°$	XeF_5^-

Intermolecular forces
ion-dipole $>$ H-bonding $>$ dipole-dipole
$\qquad\qquad\qquad\qquad\qquad \approx$ dispersion
$> 50 kJ/mol \quad \approx 25 kJ/mol \quad \approx 10 kJ/mol$

Only for charged molecules: ion-ion & ion-dipol interaction
For neutral molecules:

A Dispersion
Induced dipole attractive at short distance

B Dipole-dipole polar molecules
Molecular dipoles interact $\Rightarrow$ attractive E_{int} over short distance

A + B = van der Waals forces
- always present
- increase with molecular size
- effected by shape

Hydrogen bonding
- in molecules with $N-H, O-H, F-H$
- N, O, F very electro negative, small $\Rightarrow$ very polar

Acid Base

Auto-ionization of water
- $2H_2O \rightleftharpoons OH^-(aq) + H_3O^+(aq)$
- $K_C = [OH^-] \cdot [H_3O^+] \equiv K_W =$ **ion-product const** $= 1.0 \cdot 10^{-14}(25°C)$

Acid-base pairs
- generic rxn of acid with H_2O:

$H_2O + AH \rightarrow H_3O^+ + A^-$ $\qquad K_A = \frac{[A^-][H_3O^+]}{[HA]}$
base $\quad$ acid $\quad$ conjugate $\quad$ conjugate
$\qquad\qquad\quad$ acid $\qquad\quad$ base

- generic rxn of base with H_2O:

$H_2O + B \rightarrow OH^- + HB^+$ $\qquad K_B = \frac{[HB^+][OH^-]}{[B]}$
acid $\quad$ base $\quad$ conjugate $\quad$ conjugate
$\qquad\qquad\qquad$ base $\qquad\quad$ acid

- amphiprotic substance: can act as both acid & base, ex: $H_2O, HCO_3^-, \cdots$
- each acid/base has its conjugate base/acid

Strength of acids and bases

- $\mathbf{pH} = -\log[H^+]$
- $\mathbf{pOH} = -\log[OH^-]$
- $pK_W = 14.00 = \mathbf{pH} + \mathbf{pOH}$
- the smaller $pK_A = -\log K_A / pK_B$, the stronger acid/base

Common-ion effect
Add common ion to manipulate acid-base equil.
Ex: $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ Add strong electrolyte:
$CH_3COONa \rightarrow$ Shifts acid-base equil left, decreasing $[H_3O^+]$

Buffer
- weak acid-base conjugate pair $HA/A^- \Rightarrow$ protect against H^+/OH^-

$HA + OH^- \rightleftharpoons A^- + H2O \qquad [H_3O^+] = K_A \frac{[HA]}{[A^-]}$

$A^- + H_3O^+ \rightleftharpoons HA + H2O$

- as long as disturbance $\ll [A^-] \wedge [HA] \Rightarrow \Delta\mathbf{pH} \approx 0$
- Henderson−Hasselbalch equation, only useful for

$\mathbf{pH} = pK_A + \log \frac{[\text{base}]}{[\text{acid}]}$ $\qquad$ [acid], [base] concentration of weak
acid/conjugate base, for $K_A \ll$ [acid], [base]

Electrochemistry

Redox equations

Acidic aqueous solution
1. divide into oxidation & reduction
2. balance
   - balance elements not H/O
   - balance O by adding H_2O
   - balance H by adding H^+
   - balance charge by adding e^-
3. multiply each half rxn to equate e^-
4. add half rxn
5. check

Basic aqueous solution
1. balance half rxns as if in acidic solution
2. add $\#H^+$ of OH^- to each side
3. multiply each half rxn to equate e^-
4. add half rxns
5. check

Batteries
Galvanic cell:

- rxns $\Delta G < 0 \Rightarrow$ can extract electric work
- anode - oxidation
- cathode - reduction

Energy & batteries
- $E_{cell}^0 =$ cell voltage at standard conditions ($298.15K$, 1atm)
- standard reduction potential $e \cdot E_{red}^0 =$ pot. energy available if reduced
- $E_{cell}^0 = E_{red}^0 - E_{ox}^0 = E_{cathode}^0 - E_{anode}^0$
- to be useful/spontaneous reaction $E_{cell}^0 > 0$
- at anode lower potential
- E_{cell}^0 is intensive
- E_{red}^0 half cell can't measured directly $\Rightarrow$ standard hydrogen electrode
- $\Delta G = -nFE_{cell}^0$

Disclaimer
No guarantee of correctness