

# Redox & Energetics Cheatsheet

## Oxidation state

The following rules allow you to work out the oxidation states for elements with complex oxidation states.

1. Any atoms in elemental form have an oxidation state of 0 ex:  $O_2$ ,  $N_2$ ,  $S_0$ ,  $Fe(s)$
2. The more electronegative elements in a compound will have a negative oxidation state, while the less electronegative elements in a compound will have a positive oxidation state. As a result of their electronegativities, some elements will almost always have certain oxidation states.
  - Alkali metals are always +1
  - Alkaline earth metals are always +2
  - Fluorine is always -1
  - Hydrogen is almost always +1 (**Exception:** metal hydrides, ex:  $NaH$ , where H is -1 because Na is +1 and the compound is neutral.)
  - Oxygen is almost always -2 (**Exceptions:** peroxides, ex  $H_2O_2$ , where O is -1 because H can only donate 1 electron and the compound is neutral; and  $F_2O$ , where O is +2 because F is the only thing more electronegative than O.
3. The sum of oxidation states in a species is equal to the net charge of the species.

## Redox reactions

### Half reactions

A generalized redox reaction  $aA_{ox} + bB_{red} \longrightarrow cC_{red} + dD_{ox}$  can also be written as two **half reactions**.

- $aA_{ox} + ne^- \longrightarrow cC_{red}$
- $bB_{red} \longrightarrow dD_{ox} + ne^-$

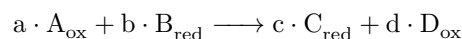
### Rules for balancing redox reactions

The following is one possible approach for systematically balancing redox reactions.

1. Separate out the two half reactions
2. Balance all elements except H & O
3. Balance O with  $H_2O$
4. Balance H with  $H^+$
5. Balance charge with  $e^-$  [check yourself here that the number of electrons transferred matches the change in oxidation state]
6. Multiply half reactions so that the number of electrons match
7. Add half reactions together

## Energetics

Consider the generalized redox reaction:



### Gibbs free energy

The Gibbs free energy of reaction ( $\Delta G_R$ ) quantifies the potential thermodynamic energy of the reaction ( $< 0 \rightarrow exothermic$ ,  $> 0 \rightarrow endothermic$ ,  $= 0 \rightarrow at equilibrium$ ) and can be calculated with:

$$\Delta G_R = \Delta G_R^0 + RT \ln \frac{[C_{red}]^c [D_{ox}]^d}{[A_{ox}]^a [B_{red}]^b} = \Delta G_R^0 + RT \ln Q$$

The standard Gibbs free energy of the reaction  $\Delta G_R^0$  is:

$$\Delta G_R^0 = \left( \sum \Delta G_f \right)_{products} - \left( \sum \Delta G_f \right)_{reactants} = -RT \ln K_{eq}$$

### Nernst potential

The redox potential ( $E$ ) or electromotive force is the electron-centric view of a redox reaction (as opposed to the reactant/product centric view inherent in the Gibbs free energy), the two are related as follows:

$$\Delta G_R = -n_{e^-} \cdot F \cdot E$$

$$\Delta G_R^0 = -n_{e^-} \cdot F \cdot E^0$$

Assuming the reaction is at 25C, plugging in the constants and switching from natural log to base 10 logarithm, this becomes:

$$E = E^0 - \frac{RT}{n_{e^-} F} \ln Q = E^0 - \frac{59.2 \text{ mV}}{n_{e^-}} \log Q$$

### Electron activity

The electron activity  $pe$  is a theoretical concept similar to  $pH$  (the proton activity) that can be calculated from the equilibrium constant ( $K_{eq}$ ) and reaction quotient ( $Q$ ) of a redox couple  $A_{ox} + e^- \rightleftharpoons A_{red}$ :

$$pe^0 = \frac{1}{n_{e^-}} \log K$$

$$pe = pe^0 - \frac{1}{n_{e^-}} \log Q$$

$E$  and  $pe$  are related by  $E = \frac{\ln 10 RT}{F} pe = 59.2 \text{ mV} \cdot pe$

### Units

- Temperature ( $T$ ): in degrees Kelvin (K) unless otherwise specified
- Gibbs free energy of reaction ( $\Delta G_R$ ): usually in kJ/mol (sometimes J/mol) where mol refers to one of the products or reactants
- Gibbs free energy of formation ( $\Delta G_f$ ): same units as  $\Delta G_R$  (kJ/mol)
- Equilibrium constant ( $K_{eq}$ ): dimensionless, technically based on activities instead of concentrations but concentrations are a reasonable approximation in dilute solutions
- Reaction quotient ( $Q$ ): dimensionless ratio of products over reactions  $\left( \prod (c_i^{n_i})_{prod} / \prod (c_i^{n_i})_{reac} \right)$ , also technically based on activities
- Nernst potential aka redox potential, electromotive force ( $E$ ): in volts (V) or milli volts (mV)
- Number of electrons ( $n_{e^-}$ ): dimensionless (usually an integer number)
- Electron Activity ( $pe$ ): dimensionless

### Constants

- The ideal gas constant (R):  $8.314 \cdot 10^{-3} \frac{\text{kJ}}{\text{K} \cdot \text{mol}}$
- The Farady constant (F):  $96.49 \frac{\text{kJ}}{\text{V} \cdot \text{mol } e^-}$