

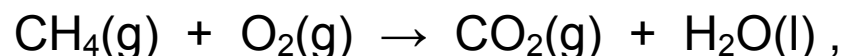
Entropy and Gibbs Free Energy

Spontaneous Processes

For every balanced reaction, there is either

- | | |
|--|------------------------------------|
| a. <i>net forward</i> reaction, | reaction is <i>spontaneous</i> |
| b. <i>net reverse</i> reaction or | reaction is <i>non-spontaneous</i> |
| c. reactants and products are in equilibrium | |

For example, the combustion of natural gas,



is spontaneous.

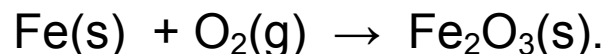
Spontaneous reactions are not all fast.

Diamond decomposes spontaneously into graphite.
Graphite has a half life of millions of years.

Another example – another exothermic spontaneous reaction.



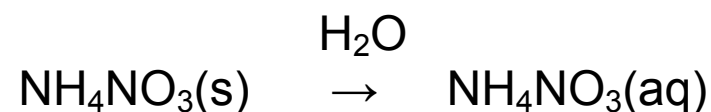
Other exothermic spontaneous reactions include the combustion of gasoline, hydrogen or any other fuel, and the oxidation of iron (rusting of steel),



The latter reaction is slow – but, unfortunately, much faster than the decomposition of diamond.

Spontaneous endothermic reactions.

For example,



Other endothermic spontaneous processes include melting of a solid above its melting point, and boiling of a liquid above its boiling point.

Ice melts spontaneously above 0°C.

The first law of thermodynamics cannot distinguish between forward and reverse processes – the *arrow of time*.

The *second law of thermodynamics* sets the arrow of time – i.e., it distinguishes spontaneous and non-spontaneous.

A clue to the origins of the second law of thermodynamics.

Argon and krypton gases mix spontaneously, as do liquid methanol and ethanol.

Ar	Ar	Ar
	Ar	Ar
Ar	Ar	Ar
Ar	Ar	
Ar		Ar

Kr	Kr	
Kr	Kr	Kr
	Kr	Kr
Kr		Kr
Kr	Kr	Kr

Kr		Ar
Ar	Kr	
		Kr
Kr	Kr	
	Ar	
Ar		Ar
	Kr	

Kr		Ar
	Kr	
Ar		Ar
	Ar	
Kr		Ar
	Ar	
Kr	Kr	Kr

Here, spontaneity is the natural tendency toward disorder.

In fact, *every spontaneous process* is just a transition to *greater disorder*.

Entropy

Disorder = greater freedom

Freedom of a system corresponds to the number of *microstates* available to the system.

A microstate corresponds to the state of every atom specified – where it is, its speed, internal energy, etc.

In the above mixing example, the volume available to each argon atom doubles when an opening appears in the boundary between the left and right containers.

The number of microstates of each argon atom increases by a factor of 2.

The number of microstates, W , of N argon atoms increases by a factor of 2^N .

$\ln W = N \ln 2$ is proportional to N – i.e., it is an extensive property.

The *Boltzmann formula*:

Entropy is given by

$$S = k_B \ln W,$$

where

$k_B = R/N_A = 1.3806 \times 10^{-23} \text{ J K}^{-1}$ is called the *Boltzmann constant*.

W is the *number of microstates*.

When argon and krypton mix, as above,

$$\begin{aligned}\Delta S_{\text{Ar}} &= k_B \ln W_{\text{fin, Ar}} - k_B \ln W_{\text{in, Ar}} \\ &= k_B \ln \frac{W_{\text{fin, Ar}}}{W_{\text{in, Ar}}} = k_B \ln 2^{N_{\text{Ar}}} \\ &= N_{\text{Ar}} k_B \ln 2 = n_{\text{Ar}} R \ln 2 \quad .\end{aligned}$$

The krypton gas experiences the same increase in entropy (with n_{Kr} replacing n_{Ar}).

The total change in entropy of krypton is

$$\begin{aligned}\Delta S &= \Delta S_{\text{Ar}} + \Delta S_{\text{Kr}} \\ &= n_{\text{Ar}} R \ln 2 + n_{\text{Kr}} R \ln 2 \\ &= 2 \text{ mol} \times R \ln 2 = 11.53 \text{ J K}^{-1} \quad ,\end{aligned}$$

if there is one mole of both argon and krypton.

This modest increase in entropy corresponds to a huge increase in number of microstates;

$$\begin{aligned}\left(\frac{W_{\text{fin}}}{W_{\text{in}}} \right)_{\text{mix}} &= \frac{W_{\text{fin, Ar}} W_{\text{fin, Kr}}}{W_{\text{in, Ar}} W_{\text{in, Kr}}} = 2^{N_{\text{Ar}} + N_{\text{Kr}}} \\ &= 2^{2 \times 6.022 \times 10^{23}}\end{aligned}$$

The reciprocal of this number is the probability of the gases unmixing.

$$\text{Probability of unmixing} = \left(\frac{W_{\text{fin}}}{W_{\text{in}}} \right)_{\text{unmix}} = 2^{-1.2044 \times 10^{24}}$$

Unmixing has the same probability as you winning the 6-49 lottery 2 billion times a day, every day for about 70 billion years – more than 5 times the current lifetime of the universe.

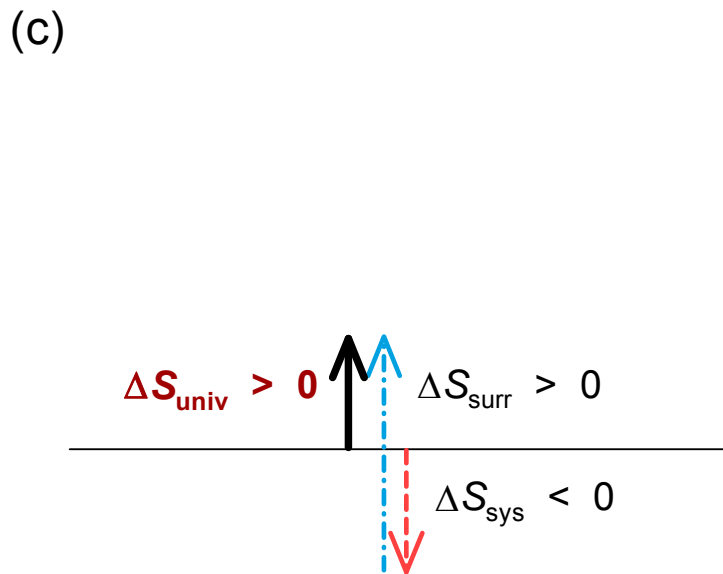
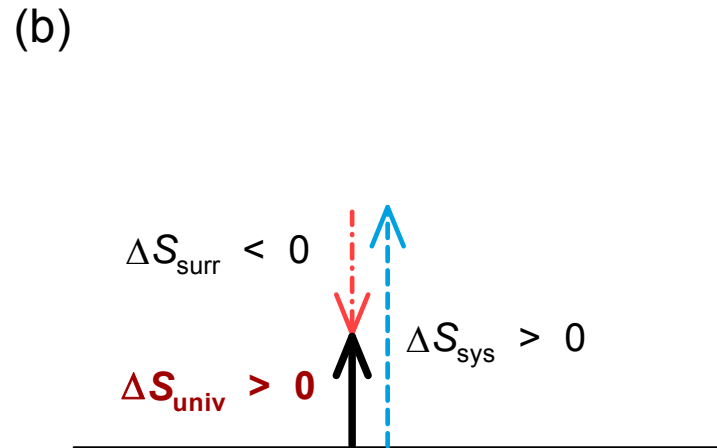
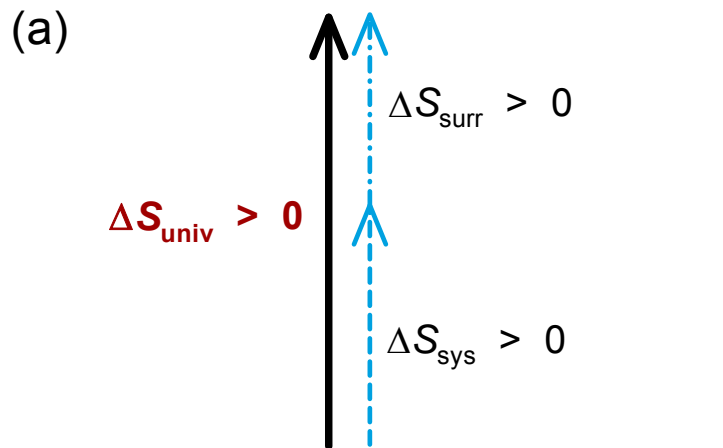
Unmixing is *non-spontaneous*.

The *second law of thermodynamics*:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

for all *spontaneous* processes.

ΔS_{surr} is the change in entropy in the surroundings due to the process.



Three types of spontaneous processes:

(a) $\Delta S_{\text{sys}} > 0$ and $\Delta S_{\text{surr}} > 0$.

(b) $\Delta S_{\text{sys}} > 0$, $\Delta S_{\text{surr}} < 0$ and $-\Delta S_{\text{sys}} < \Delta S_{\text{surr}}$.

(c) $\Delta S_{\text{sys}} < 0$, $\Delta S_{\text{surr}} > 0$ and $-\Delta S_{\text{surr}} < \Delta S_{\text{sys}}$.

Properties of Entropy

Like energy and enthalpy, entropy is *extensive*.

Consider two identical systems, each with entropy, S .
The combined entropy of the two systems is $2 S$.

Molar entropy, expressed in $\text{J K}^{-1} \text{mol}^{-1}$, is an intensive quantity, characteristic of a substance with specific temperature and pressure.

Molar entropies of substances, under standard conditions (25°C and 1 bar pressure), are tabulated along with enthalpies of formation.

Entropy depends on *temperature* and *pressure*.

Thermodynamics defines entropy via

$$\Delta S = q / T ,$$

q is the heat flow into the system.

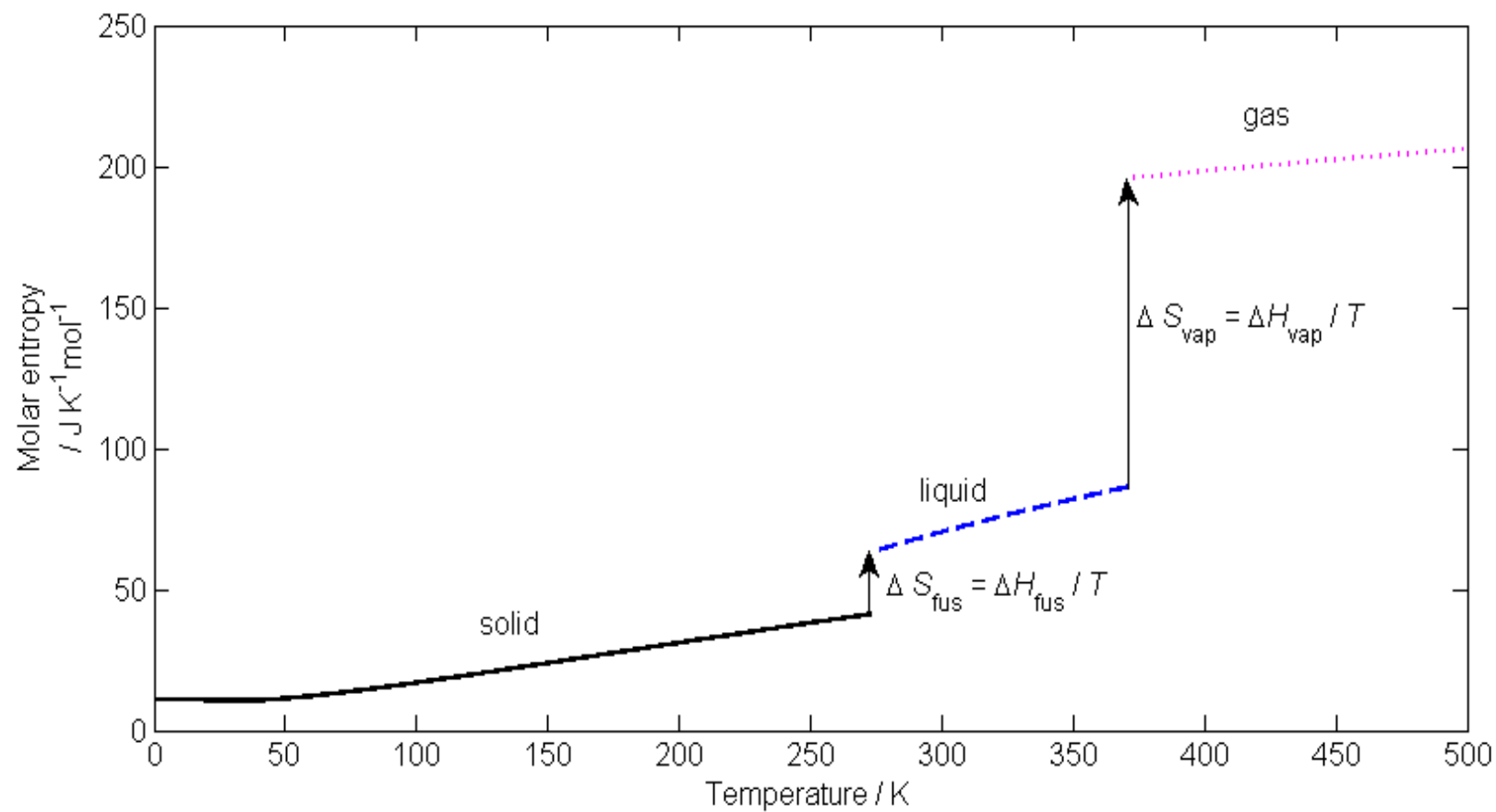
Positive q *increases* entropy.

Negative q *decreases* entropy.

Entropy increases with increasing temperature.

It also increases when a solid melts or a liquid boils

Melting and boiling are endothermic ($q = \Delta H > 0$).



The molar entropy of water at 1 bar pressure.

Consider the molar entropy for water at 1 bar pressure, from 0 to 500 K.

The *third law of thermodynamics* states that a pure, perfect crystalline substance at zero Kelvin has zero entropy.

This follows from Boltzmann's formula, since a pure, perfect crystal at absolute zero has just one microstate – the quantum ground state of the substance.

At zero Kelvin, ice is not a perfect crystal. Its entropy is not zero. But it can be calculated.

There is residual entropy associated with disorder in the arrangement of hydrogen atoms within the crystal – due to hydrogen bonding.

(1) When the solid is heated, intramolecular and intermolecular vibrations increase in magnitude.

Entropy of the solid increases with increasing temperature.

(2) When the solid melts, entropy increases discontinuously at the melting temperature. Molecules have more freedom in the liquid where they are not confined to lattice positions.

$$\Delta S_{\text{fus}} > 0$$

(3) Vibrations in the liquid increase in magnitude with increasing temperature.

Entropy of the liquid increases with increasing temperature.

(4) When the liquid boils, there is a large increase in entropy (disorder). Molecules in the gas are free to explore the entire volume of the gas container, rather than sitting in a pool at the bottom of the container.

$$\Delta S_{\text{vap}} > 0$$

$$S_{\text{sol}} < S_{\text{liq}} \ll S_{\text{gas}}$$

(5) Molar entropy continues to increase with temperature, for the gas, as intramolecular vibrations, translations and rotations become more energetic and consequently more disordered.

The heat required to melt 1 mol of a solid, at fixed pressure, is just the enthalpy of fusion. Therefore,

$$\Delta S_{\text{fus}} = \Delta H_{\text{fus}} / T$$

Similarly, the heat required to boil 1 mol of a liquid is the enthalpy of vaporization, and

$$\Delta S_{\text{vap}} = \Delta H_{\text{vap}} / T$$

Standard Molar Entropy

The *standard molar entropy*, S° , of a substance is the entropy of 1 mol of the substance at 25°C, under *standard conditions* – specifically, 1 bar pressure and 1 mol L⁻¹ concentration for aqueous species.

For example, $S^\circ[\text{H}_2\text{O}(\text{l})] = 70.0 \text{ J K}^{-1}\text{mol}^{-1}$ and $S^\circ[\text{H}_2\text{O}(\text{g})] = 188.7 \text{ J K}^{-1}\text{mol}^{-1}$.

$$\begin{aligned}\Delta S^\circ_{\text{vap}}[\text{H}_2\text{O}] &= S^\circ[\text{H}_2\text{O}(\text{g})] - S^\circ[\text{H}_2\text{O}(\text{l})] = 188.7 - 70.0 \text{ J K}^{-1}\text{mol}^{-1} \\ &= 118.7 \text{ J K}^{-1}\text{mol}^{-1}\end{aligned}$$

(1) Consider two substances in the same phase, consisting of small molecules of the same complexity (e.g. both diatomic). The substance with the larger molar mass has the greater molar entropy.

Due to the *uncertainty principle* of *quantum mechanics*.

One microstate of a heavier molecule corresponds to a smaller volume in space than a microstate of a lighter molecule.

There are more microstates available to a heavier molecule confined to the same volume.

For example, $S^\circ[\text{H}_2(\text{g})] = 130.6 \text{ J K}^{-1}\text{mol}^{-1}$ and $S^\circ[\text{O}_2(\text{g})] = 205.0 \text{ J K}^{-1}\text{mol}^{-1} > S^\circ[\text{H}_2(\text{g})]$.

(2) More complex molecules have larger standard molar entropy. For example,

$$S^{\circ}[\text{NO}(\text{g})] < S^{\circ}[\text{NO}_2(\text{g})] < S^{\circ}[\text{N}_2\text{O}_4(\text{g})] \quad .$$

Complex molecules have more types of motion.

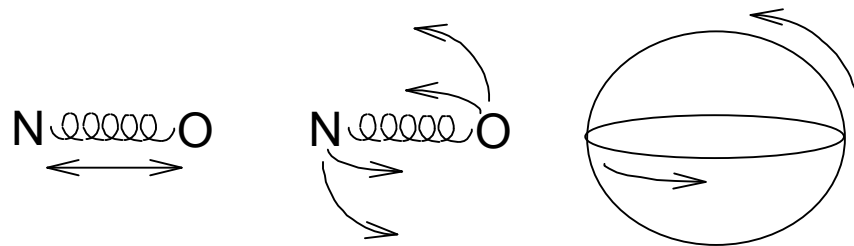
For example,

NO has 1 vibration and 2 rotations (rotation about the axis of a linear molecule does not count).

NO₂ has 3 vibrations (2 distinct stretches and one bend) and three rotations.

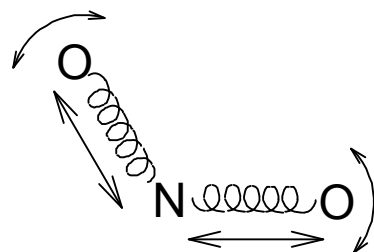
N₂O₄ has 12 vibrations (5 stretches and 7 bends).

Each of these motions stores thermal energy and contributes to the total number of microstates, and the total molar entropy.



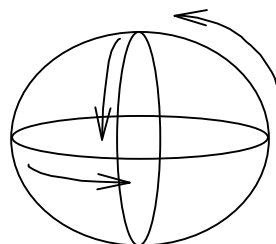
1 stretch vibration

2 rotations

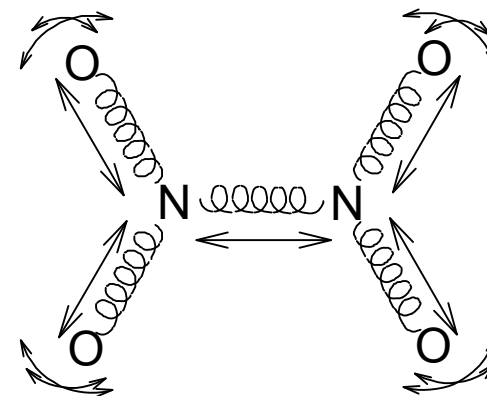


3 vibrations:

2 stretches and 1 bend



3 rotations



12 vibrations:

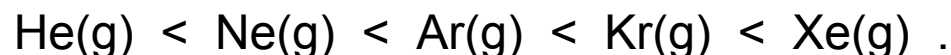
5 stretches and 7 bends

3 rotations

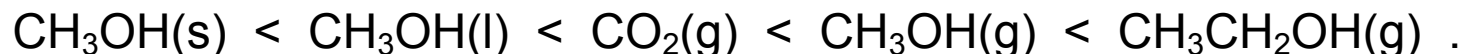
Example: Order the following sets of substances according to increasing molar entropy.

- (a) Ne(g), He(g), Xe(g), Ar(g) and Kr(g)
- (b) CH₃CH₂OH(g), CH₃OH(g), CH₃OH(l), CH₃OH(s) and CO₂(g).
- (c) CO₂(g), CO₂(s), CS₂(g) and CS₂(s).

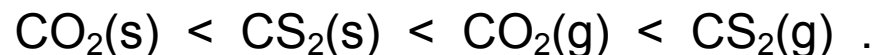
(a) According to increasing molar entropy,



(b) According to increasing molar entropy,



(c)



Entropy of Reaction

Entropy is a state function.

The standard *entropy of reaction*:

$$\Delta S^{\circ} = \sum_{\text{products, P}} c_{\text{P}} S^{\circ}[\text{P}] - \sum_{\text{reactants, R}} c_{\text{R}} S^{\circ}[\text{R}]$$

where c_{P} and c_{R} are the stoichiometric coefficients of product, P, and reactant, R, respectively.

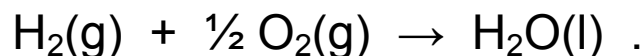
This is analogous to the formula for the enthalpy of reaction in terms of enthalpies of formation.

However, whereas elements in their standard state have zero standard enthalpy of formation, they do not have zero standard molar entropy.

Example: Determine the standard entropy of formation of liquid water, given the following data:

Compound	S° (J K ⁻¹ mol ⁻¹)
H ₂ (g)	130.6
O ₂ (g)	205.0
H ₂ O(l)	70.0

The formation reaction for liquid water is the reaction that forms one mole of liquid water:



The associated standard entropy of reaction is given in terms of the tabulated absolute entropies:

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{H}_2\text{O}(\text{l})] - \{ S^\circ[\text{H}_2(\text{g})] + \frac{1}{2} S^\circ[\text{O}_2(\text{g})] \} \\ &= 70.0 - (130.6 + \frac{1}{2} \times 205.0) \text{ J K}^{-1}\text{mol}^{-1}\end{aligned}$$

$$= -163.1 \text{ J K}^{-1}\text{mol}^{-1}$$

In the formation reaction of liquid water, 1 ½ moles of gas react to form 1 mole of liquid,

$$\Delta n_{\text{gas}} = -1 \frac{1}{2}$$

Since gases have much larger standard molar entropy than solids or liquids, the entropy change is *negative* with a relatively large magnitude.

In general,

(1) If $\Delta n_{\text{gas}} < 0$, then ΔS is *negative* and large in magnitude – roughly in proportion to Δn_{gas} . If $\Delta n_{\text{gas}} > 0$, then ΔS is *positive* and large in magnitude.

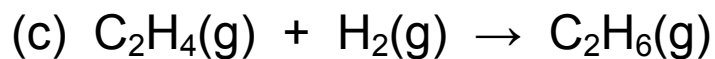
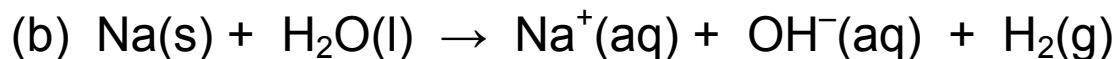
(2) If $\Delta n_{\text{gas}} = 0$, the sign of ΔS depends on Δn_{aq} or Δn_{liq} , the changes (products – reactants) in the number of moles of aqueous and liquid components, respectively.

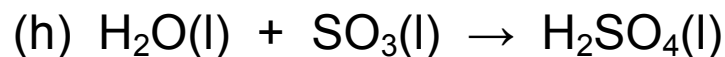
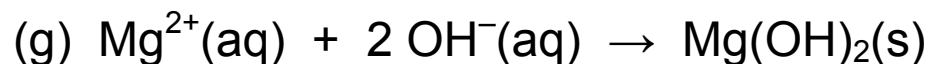
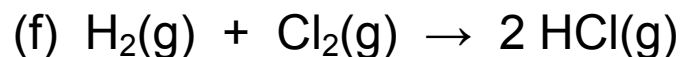
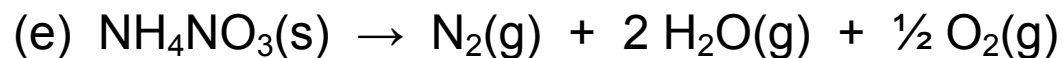
If $\Delta n_{\text{aq}} > 0$, ΔS is intermediate (in magnitude) and positive. If $\Delta n_{\text{aq}} < 0$, ΔS is intermediate and negative.

If $\Delta n_{\text{gas}} = 0$ and $\Delta n_{\text{aq}} = 0$, Δn_{liq} determines the sign of ΔS . Otherwise, it is intermediate in magnitude.

(3) If $\Delta n_{\text{gas}} = 0$, $\Delta n_{\text{aq}} = 0$ and $\Delta n_{\text{liq}} = 0$, then ΔS is small and its sign cannot be determined by inspection of the balanced reaction.

Example: Label the following reactions according to whether ΔS is (i) positive and large in magnitude, (ii) negative and large in magnitude, (iii) positive and intermediate in magnitude, (iv) negative and intermediate in magnitude, or (v) small in magnitude. Order the reactions according to increasing ΔS .





(a) No gases and $\Delta n_{\text{aq}} = +2$. ΔS is *positive* and *intermediate* in magnitude.

(b) $\Delta n_{\text{gas}} = +1$ and $\Delta n_{\text{aq}} = +2$. ΔS is *positive* and *large* in magnitude.

(c) $\Delta n_{\text{gas}} = -1$. ΔS is *negative* and *large* in magnitude.

(d) No gases and $\Delta n_{\text{aq}} = +3$. ΔS is *positive* and *intermediate* in magnitude – larger than reaction (a) though, as $\Delta n_{\text{aq}} = +2$ in that case.

(e) $\Delta n_{\text{gas}} = +3 \frac{1}{2}$. ΔS is *positive* and *large* in magnitude – larger than reaction (b).

(f) $\Delta n_{\text{gas}} = 0$ and there are no aqueous or liquid reactants or products. ΔS is *small* in magnitude.

(g) No gases and $\Delta n_{\text{aq}} = -3$. ΔS is *negative* and *intermediate* in magnitude.

(h) No gases and $\Delta n_{\text{liq}} = -1$. ΔS is *negative* and *intermediate* in magnitude – smaller than reaction (g) because aqueous components typically have more entropy than pure liquid components.

The order of reactions according to increasing ΔS (from negative and large in magnitude to positive and large in magnitude) is given by

$$c < g < h < f < a < d < b < e .$$

The Second Law of Thermodynamics

Processes that *occur* are such that

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 .$$

The criterion for spontaneity

ΔS_{surr} arises because there may be heat transfer *to* or *from* the system – i.e., *from* or *to* the surroundings.

Heat transfer changes the entropy of the surroundings.

For constant temperature processes,

$$\Delta S_{\text{surr}} = q_{\text{surr}} / T$$

Since

$$q_{\text{surr}} = -q_{\text{sys}} ,$$

$$\Delta S_{\text{surr}} = -q_{\text{sys}} / T$$

For constant pressure processes,

$$q_{\text{sys}} = \Delta H_{\text{sys}}$$

and

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

The criterion for spontaneity now takes the form,

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}} / T > 0 ,$$

for *spontaneous processes* occurring at *constant temperature* and *pressure*.

This is why so many spontaneous processes are exothermic.

Negative ΔH_{sys} corresponds to heat released into the surroundings - increasing the entropy of the surroundings.

Example: Determine ΔS_{univ} for the formation reaction of one mole of liquid water, at 25°C, given

$$\Delta S_f^\circ [\text{H}_2\text{O}(\text{l})] = -163.1 \text{ J K}^{-1}\text{mol}^{-1}$$

and

$$\Delta H_f^\circ [\text{H}_2\text{O}(\text{l})] = -285.8 \text{ kJ mol}^{-1} .$$

Is the reaction of hydrogen and oxygen to form liquid water spontaneous at 25°C?

The entropy change of the system for the formation reaction of one mole of liquid water, at 25°C, is just the standard entropy of formation of liquid water.

$$\Delta S_{\text{sys}} = \Delta S_{\text{f}}^{\circ}[\text{H}_2\text{O}(\text{l})] = -163.1 \text{ J K}^{-1}\text{mol}^{-1}$$

Here,

$$\Delta H_{\text{sys}} = \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(\text{l})] = -285.8 \text{ kJ mol}^{-1}$$

and

$$\begin{aligned}\Delta S_{\text{surr}} &= -\Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(\text{l})] / T = 285.8 \text{ kJ mol}^{-1} / 298.15 \text{ K} \\ &= 958.6 \text{ J K}^{-1}\text{mol}^{-1} .\end{aligned}$$

Altogether,

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= -163.1 + 958.6 \text{ J K}^{-1}\text{mol}^{-1} = 796 \text{ J K}^{-1}\text{mol}^{-1} .\end{aligned}$$

Since $\Delta S_{\text{univ}} > 0$, this process is *spontaneous* at 25°C and 1 bar pressure.

Gibbs Free Energy

The criterion for spontaneity, for constant temperature and pressure processes, in terms of changes to the system:

$$\Delta S_{\text{sys}} - \Delta H_{\text{sys}} / T > 0$$

or

$$\Delta S - \Delta H / T > 0$$

Rearranging gives

$$\Delta H - T \Delta S < 0$$

or

$$\Delta (H - T S) < 0$$

The *Gibbs free energy*:

$$G = H - T S$$

The criterion for spontaneity of constant T and P processes now takes the form,

$$\Delta G < 0$$

Since

$$\Delta G = \Delta H - T \Delta S$$

we also have

$$\Delta H < T \Delta S$$

Sign of ΔH	Sign of ΔS	Sign of ΔG	Spontaneous?
– exothermic	+	– at <i>all</i> temperatures	<i>spontaneous</i>
	–	– at <i>low</i> temperature + at high temperature	<i>spontaneous</i> non-spontaneous
+ endothermic	+	+ at low temperature – at <i>high</i> temperature	non-spontaneous <i>spontaneous</i>
	–	+ at all temperatures	non-spontaneous

Exothermic processes with *positive* change in (system) *entropy* are *always* spontaneous – i.e., spontaneous at *all* temperatures.

These processes include the combustion of ethane (or any larger hydrocarbon), the reaction of sodium and water, and the decomposition of hydrogen peroxide.

The *reverse* of such processes, *endothermic* processes with *negative* entropy change, are *never* spontaneous.

Exothermic processes with *negative* entropy change, are spontaneous only *below* the *crossover temperature*,

$$T_{\text{cross}} = \Delta H / \Delta S$$

Examples include the rusting of iron (or any metal), freezing of any liquid, and condensation of any gas. A liquid freezes only below its freezing point – the melting point of solid.

The crossover temperature of the freezing process is the *melting point*.

The crossover temperature of the condensation process is the *boiling point*.

Endothermic processes with *positive* change in entropy are the *reverse* of these processes. They are spontaneous only above T_{cross} .

For example, a liquid boils only above its *boiling point* – the crossover temperature of the boiling process (the reverse of condensation).

Standard Gibbs Free Energy of Reaction

Standard Gibbs free energy of reaction – for any reaction – can be determined from tabulated *standard Gibbs free energies of formation*.

$$\Delta G^{\circ} = \sum_{\text{products, P}} c_{\text{P}} \Delta G_f^{\circ}[\text{P}] - \sum_{\text{reactants, R}} c_{\text{R}} \Delta G_f^{\circ}[\text{R}]$$

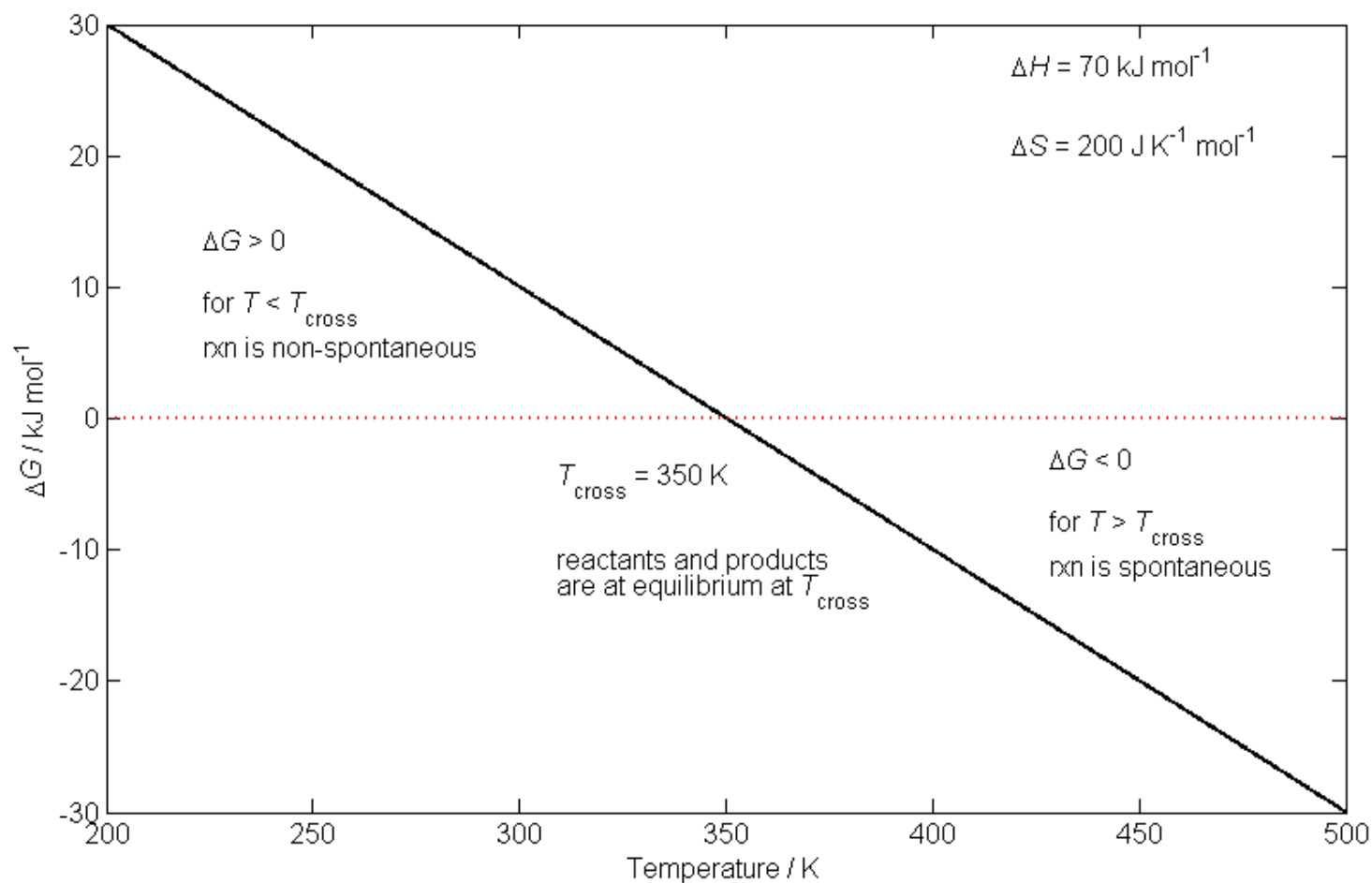
At 25°C, and under *standard conditions* – all gases at 1 bar partial pressure and solutes at 1 mol L⁻¹ concentration.

At other temperatures, or under non-standard conditions, the Gibbs free energy of reaction is generally different.

Temperature Dependence of ΔG°

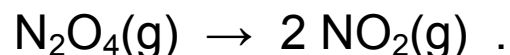
$$\Delta G = \Delta H^\circ - T \Delta S^\circ$$

We treat ΔH° and ΔS° as temperature independent.



The case of an endothermic reaction ($\Delta H > 0$) with $\Delta S > 0$.

Example: Consider the decomposition of dinitrogen tetroxide:



Data at 25°C:

Compound	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)
N ₂ O ₄ (g)	11.1	99.8
NO ₂ (g)	33.2	51.3

- (a) Determine the standard Gibbs free energy of this decomposition reaction at 25°C. Is it spontaneous at 25°C?
- (b) Determine the standard Gibbs free energy of the decomposition at 50°C. Is it spontaneous at 50°C?
- (c) Estimate the crossover temperature for the decomposition of dinitrogen tetroxide under standard conditions (1 bar partial pressure of both gases).

(a) At 25°C,

$$\begin{aligned}\Delta G^{\circ} &= 2\Delta G_f^{\circ}[\text{NO}_2(\text{g})] - \Delta G_f^{\circ}[\text{N}_2\text{O}_4(\text{g})] \\ &= 2 \times 51.3 - 99.8 \text{ kJ mol}^{-1} \\ &= 2.8 \text{ kJ mol}^{-1}\end{aligned}$$

The decomposition of dinitrogen tetroxide is *not* spontaneous at 25°C.

(b) Also at 25°C,

$$\begin{aligned}\Delta H^{\circ} &= 2\Delta H_f^{\circ}[\text{NO}_2(\text{g})] - \Delta H_f^{\circ}[\text{N}_2\text{O}_4(\text{g})] \\ &= 2 \times 33.2 - 11.1 \text{ kJ mol}^{-1} \\ &= 55.3 \text{ kJ mol}^{-1} ,\end{aligned}$$

Therefore,

$$\begin{aligned}
 \Delta S^{\circ} &= \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \\
 &= \frac{55.3 - 2.8 \text{ kJ mol}^{-1}}{298.15 \text{ K}} \times 1000 \text{ J kJ}^{-1} \\
 &= 176.1 \text{ J K}^{-1} \text{ mol}^{-1} ,
 \end{aligned}$$

The Gibbs free energy of reaction at 50°C (another temperature) – assuming enthalpy and entropy of reaction are temperature independent:

$$\begin{aligned}
 \Delta G^{\circ} &= \Delta H^{\circ} - T \Delta S^{\circ} \\
 &= 55.3 \text{ kJ mol}^{-1} - 323.15 \text{ K} \times 176.1 \text{ J K}^{-1} \text{ mol}^{-1} / 1000 \text{ J kJ}^{-1} \\
 &= -1.6 \text{ kJ mol}^{-1} .
 \end{aligned}$$

The reaction is spontaneous at 50°C.

(c) The crossover temperature, under standard conditions, is given by

$$\begin{aligned}T_{\text{cross}} &= \Delta H^{\circ} / \Delta S^{\circ} \\&= 55.3 \text{ kJ mol}^{-1} \times 1000 \text{ J kJ}^{-1} / 176.1 \text{ J K}^{-1} \text{ mol}^{-1} \\&= 314. \text{ K} , \\&\text{or } 41^{\circ}\text{C}.\end{aligned}$$

Gibbs Free Energy and Equilibrium

$$\Delta G = 0 \quad \text{equilibrium conditions}$$

Equilibrium is achieved under standard conditions at the crossover temperature.

At any temperature, reactions including *gases* and *solutions* can achieve equilibrium with both reactant and product present.

Under *non-standard conditions*,

$$\Delta G = \Delta G^\circ + R T \ln Q$$

The extra term accounts for the dependence of the entropy of reactants and products on their activities – lower activity means more freedom.

A *dilute* solute has *higher* entropy per mole than the concentrated solute,
and *lower* Gibbs free energy.

A *low* pressure gas has *higher* entropy per mole than the high pressure gas,
and *lower* Gibbs free energy.

At *equilibrium*, $Q = K$ and

$$\Delta G = \Delta G^\circ + R T \ln Q = 0 .$$

Therefore,

$$\Delta G^\circ + R T \ln K = 0$$

or

$$\Delta G^\circ = -R T \ln K$$

Under *non-standard conditions*,

$$\Delta G = -R T \ln K + R T \ln Q$$

or

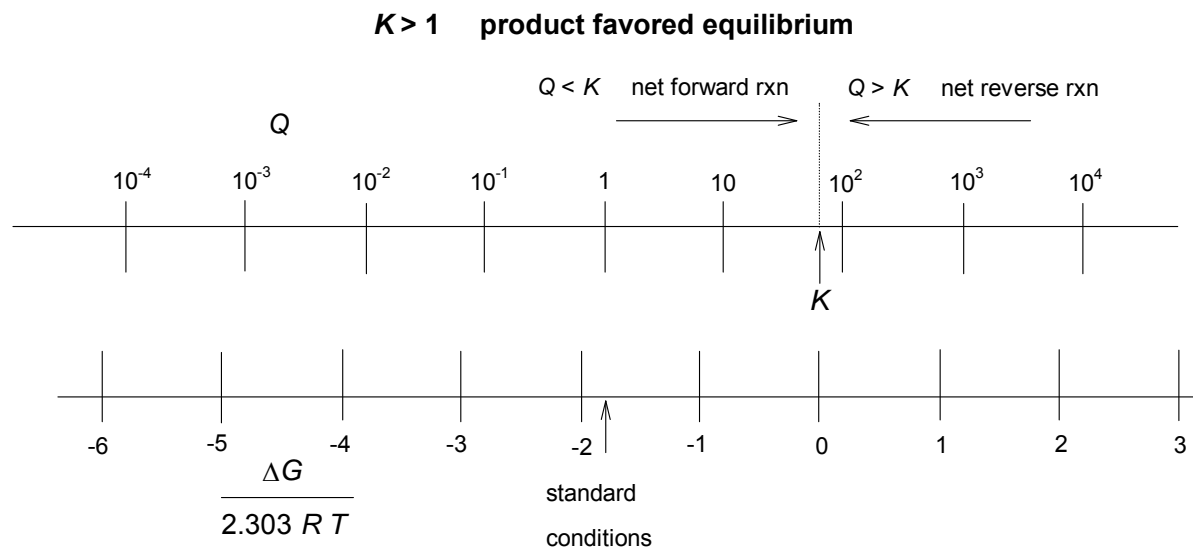
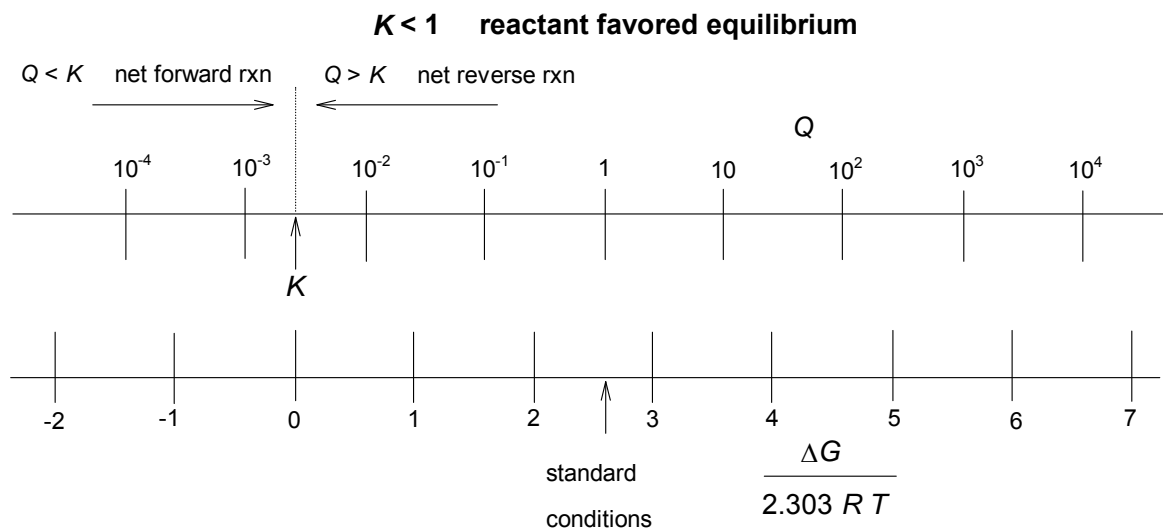
$$\Delta G = R T \ln \left(\frac{Q}{K} \right)$$

If $Q < K$, there is net *forward* reaction. This corresponds to $\Delta G < 0$.

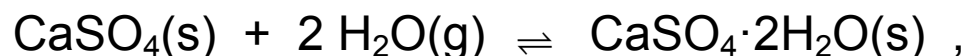
If $Q < K$, there is net *reverse* reaction. This corresponds to $\Delta G > 0$.

The *equilibrium constant* in terms of ΔG° :

$$K = \exp\left(-\frac{\Delta G^\circ}{R T}\right)$$



Example: Consider the hydration of anhydrous calcium sulfate:



for which $\Delta H^\circ = -104.9 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -290.2 \text{ J K}^{-1} \text{ mol}^{-1}$, at 25°C . Calcium sulfate acts as a *desiccant* because of this reaction – specifically, it removes water vapor from air.

- (a) Determine ΔG° for this reaction at 25°C . Is it spontaneous under standard conditions – i.e. water vapor with 1 bar partial pressure?
- (b) What is the equilibrium constant for hydration of calcium sulfate at 25°C ?
- (c) Determine ΔG , at 25°C , if the partial pressure of water is 3.2 kPa. A water partial pressure of 3.2 kPa corresponds to 100% relative humidity at 25°C – i.e., water vapor in equilibrium with liquid water at that temperature. Is the hydration reaction spontaneous with this partial pressure of water?
- (d) At what partial pressure of water vapor is the hydration reaction at equilibrium, at 25°C ?

(a) The Gibbs free energy of reaction at 25°C is given by

$$\begin{aligned}\Delta G &= \Delta H - T \Delta S = -104.9 \text{ kJ mol}^{-1} - 298.15 \times (-290.2 \text{ J K}^{-1} \text{ mol}^{-1}) / \\ &\quad (1000 \text{ J kJ}^{-1}) \\ &= -18.3_8 \text{ kJ mol}^{-1} .\end{aligned}$$

(b) The equilibrium constant at 25°C is given by

$$\begin{aligned}K &= \exp\left(-\frac{\Delta G^\circ}{R T}\right) = \exp\left(-\frac{-18.3_8 \text{ kJ mol}^{-1} \times 1000 \text{ J kJ}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}\right) \\ &= \exp\left(\frac{18.3_8 \text{ kJ mol}^{-1} \times 1000 \text{ J kJ}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}\right) = 1.66 \times 10^3 .\end{aligned}$$

(c) The reaction quotient for this reaction is

$$\begin{aligned} Q &= \frac{1}{P_{\text{H}_2\text{O}}^2} \\ &= \frac{1}{\left(\frac{3.2 \text{ kPa}}{100. \text{ kPa}}\right)^2} = 9.7_7 \times 10^2 \text{ under the given conditions.} \end{aligned}$$

The Gibbs free energy of reaction for this partial pressure of water is

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= -18.3_8 \text{ kJ mol}^{-1} + \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{1000 \text{ J kJ}^{-1}} \ln(9.7_7 \times 10^2) \\ &= -1.3 \text{ kJ mol}^{-1} \end{aligned}$$

Since this ΔG is negative, the hydration reaction is spontaneous under the given conditions – i.e., anhydrous calcium sulfate will spontaneously hydrate when exposed to water saturated air at 25°C.

(d) Setting $Q = K$ gives

$$Q = \frac{1}{P_{\text{H}_2\text{O}}^2} = K = 1.66 \times 10^3$$

or

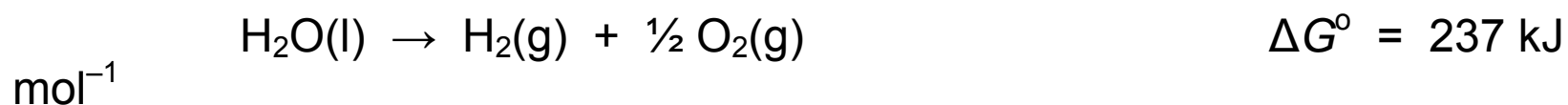
$$\begin{aligned} P_{\text{H}_2\text{O}} &= \frac{1}{\left(1.66 \times 10^3\right)^{1/2}} = 0.0245 \text{ bar} \\ &= 100.0 \text{ kPa bar}^{-1} \times 0.0245 \text{ bar} = 2.45 \text{ kPa} . \end{aligned}$$

Coupled Reactions

A *non-spontaneous* reaction can be coupled to a *spontaneous* reaction, such that the combined process is *spontaneous*.

We can *drive* a non-spontaneous reaction.

For example, electrolysis of water produces $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ by coupling



to a DC electrical power supply.

Coupled reactions abound in life.

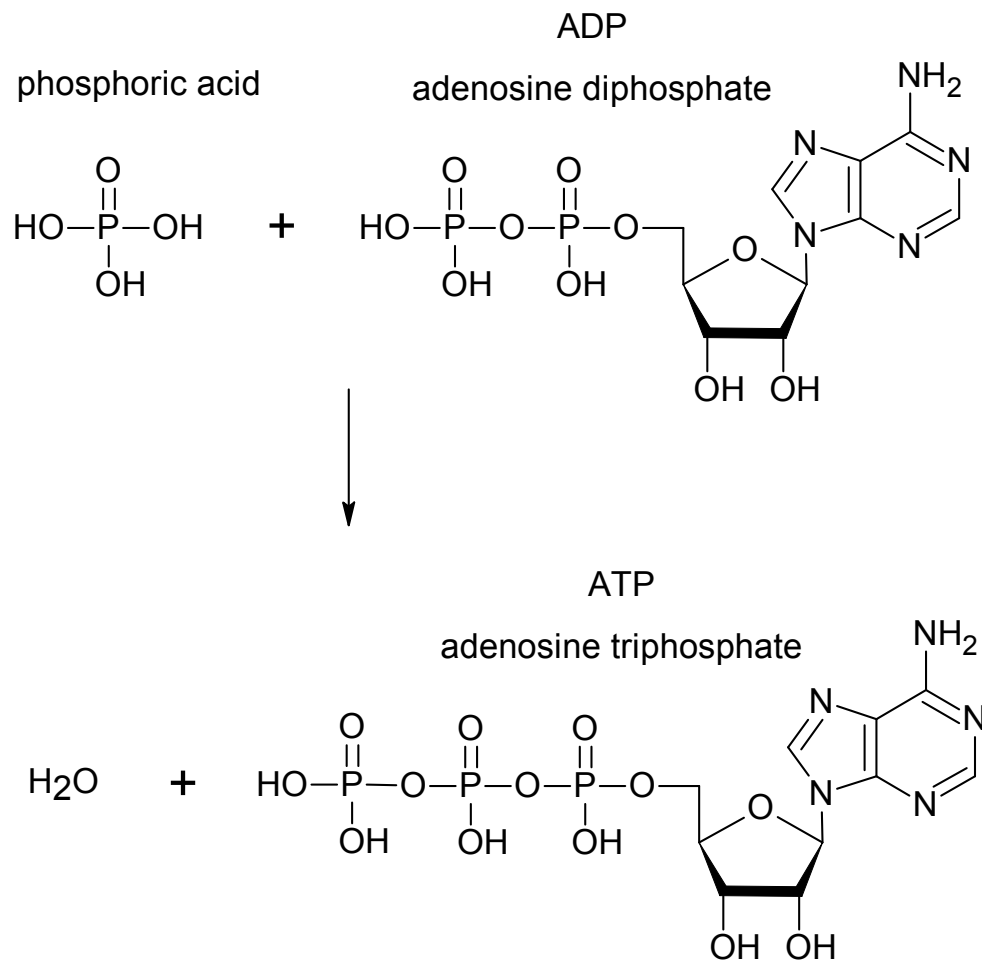
Metabolism of glucose is a spontaneous process:



This occurs through a series of steps – *cellular respiration*.

The Gibbs free energy liberated is stored in ATP molecules (adenosine triphosphate), as the spontaneous oxidation of glucose drives the otherwise non-spontaneous *condensation* reaction,





The *condensation* of phosphoric acid and ADP (adenosine diphosphate) to form ATP (adenosine triphosphate). The reverse reaction is the *hydrolysis* of ATP.

Under conditions in the body, the Gibbs free energy of the above condensation reaction is closer to 50 kJ mol^{-1} – it depends on the concentration of Mg^{2+} .

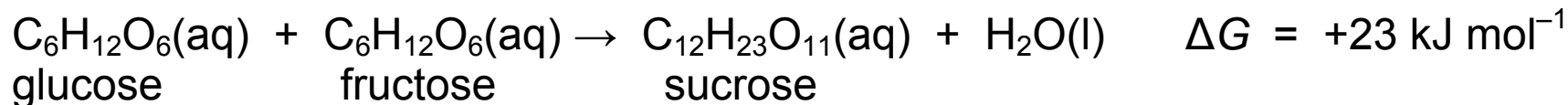
Typically, about 30 ATP molecules are produced in the net cellular respiration of one glucose molecule.

The net Gibbs free energy change of cellular respiration:

$$30 \times 50 - 2880 \text{ kJ mol}^{-1} = -1380 \text{ kJ mol}^{-1} < 0$$

The spontaneous *hydrolysis* of ATP to form ADP is coupled to other non-spontaneous reactions, via enzymes and other proteins.

For example, the non-spontaneous (by itself) condensation of glucose and fructose is driven by free energy derived from hydrolysis of ATP.



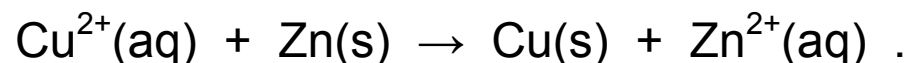
Electrochemistry

Electron Transfer Reactions

Redox reactions are *electron transfer reactions*.

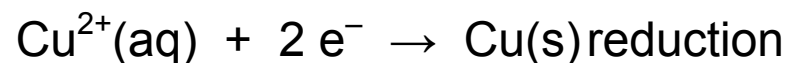
Electrons are transferred from the reducing agent to the oxidizing agent.

For example,

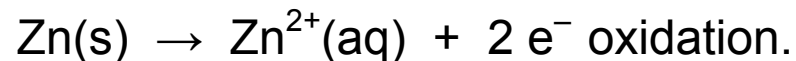


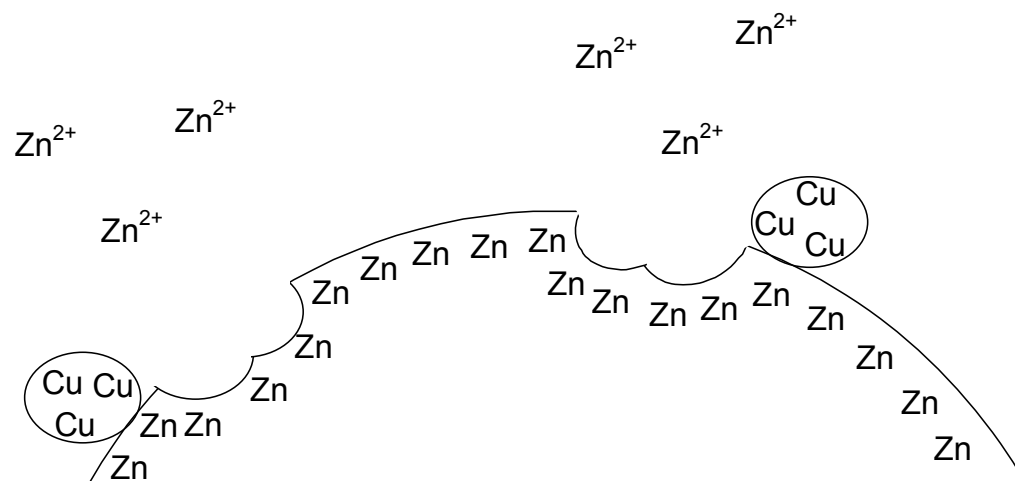
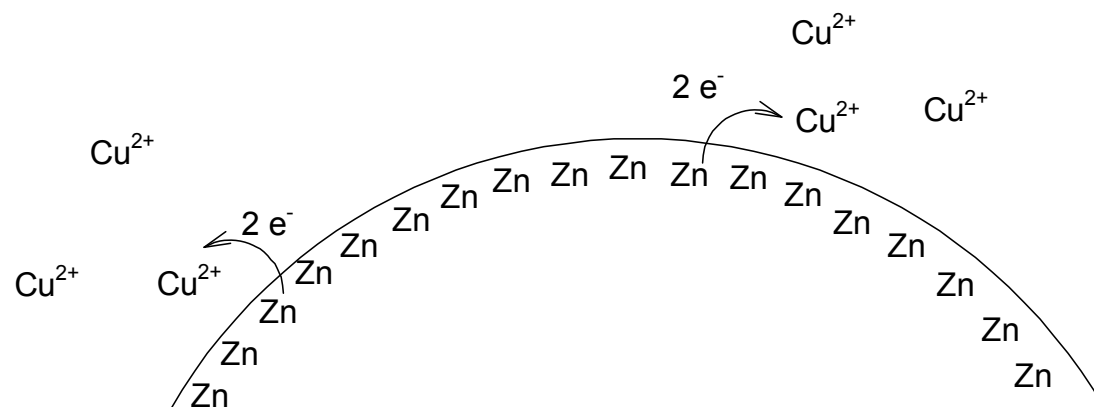
Two electrons are transferred from a zinc atom to a copper II ion to give a zinc ion and a copper atom.

The *half reactions* are written as



and





Electrochemical Cells

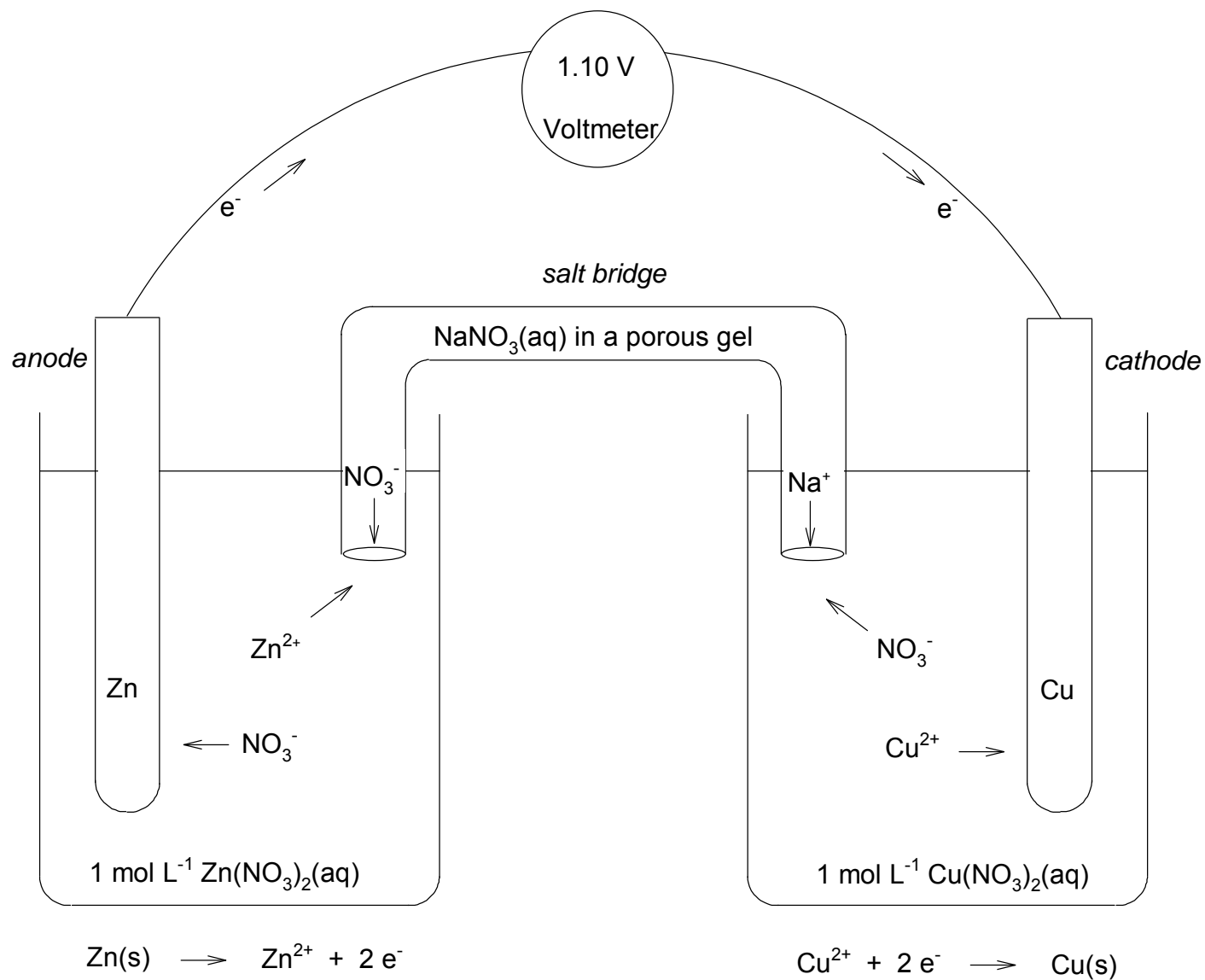
In an electrochemical cell – also known as a Galvanic or Voltaic cell – electrons released by the oxidation half reaction travel through a wire – and do electrical work – before they are consumed by the reduction half reaction.

The half reactions take place at the surface of metallic electrodes:

- (1) *oxidation* occurs at the *anode*
- (2) *reduction* occurs at the *cathode*.

Electrons liberated by the oxidation half reaction at the anode travel through wires to the cathode, and are consumed there by the reduction half reaction.

The zinc-copper electrochemical cell under standard conditions – i.e.,
 1 mol L^{-1} concentration of $\text{Cu}^{2+}(\text{aq})$ and $\text{Zn}^{2+}(\text{aq})$.



Redox half reactions take place in the *half cells* on the **left** (**oxidation** at the **anode**) and on the **right** (**reduction** at the **cathode**).

The half cells are connected by a wire, between anode and cathode, and a *salt bridge* – required to complete the circuit.

Cell Diagrams

The zinc-copper cell is represented by the *cell diagram*,



The anode is on the left.

The cathode is on the right.

Vertical lines denote phase boundaries.

Here, they separate the solid and aqueous reactants and products.

Double vertical lines denote the salt bridge.

Sometimes the cell diagram is written with spectator ions left out. For the zinc-copper cell,



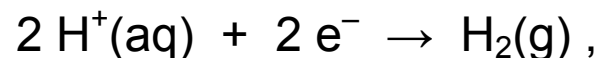
In the zinc-copper cell, the reactant is the anode, while the product is the cathode.

Sometimes there are no metals among the reactants and products in a half reaction.

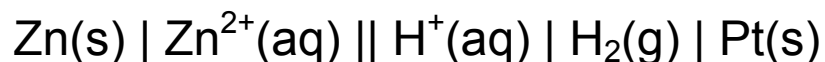
An inert metal such as platinum serves as anode and/or cathode, as required - an *inactive* electrode.

In the zinc-hydrogen cell, under standard conditions, the *hydrogen electrode* acts as cathode.

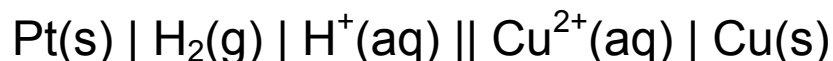
Reduction half reaction:



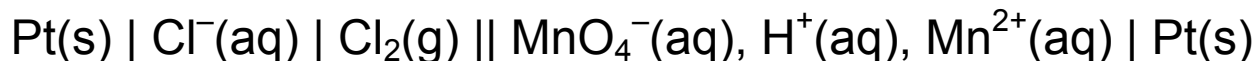
Cell diagram:



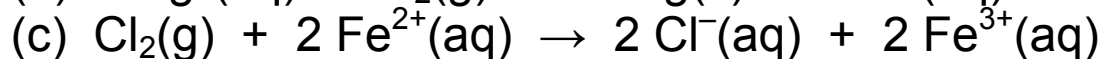
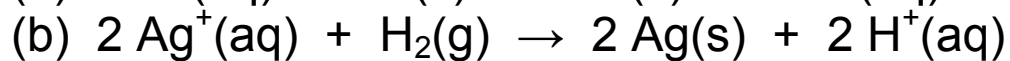
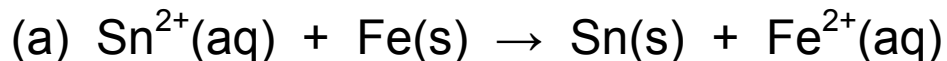
The hydrogen-copper cell diagram:



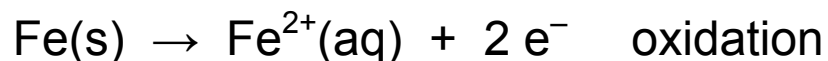
The chlorine-permanganate cell diagram:



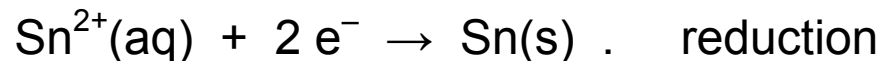
Example: Write the cell diagrams for electrochemical cells based on the net ionic equations:



(a) Iron atoms lose electrons, while tin ions gain electrons. The half reactions are



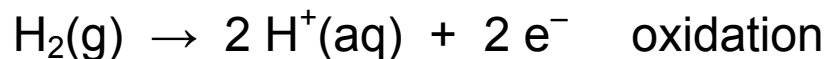
and



Metallic iron provides the reactant in the oxidation half reaction, and serves as anode. Similarly, metallic tin is the product of the reduction half reaction, and provides the cathode. Both half cells have two phases – metallic solid and aqueous. The cell diagram is



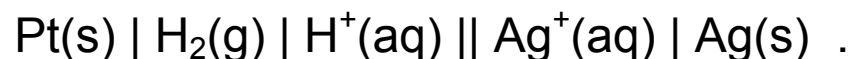
(b) Hydrogen molecules lose electrons, while silver ions gain electrons. The half reactions are



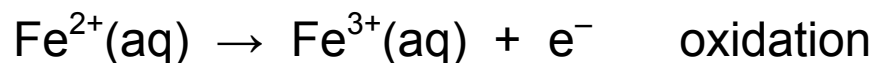
and



An inactive anode is required – use Pt(s). Silver metal provides the cathode. The cell diagram is



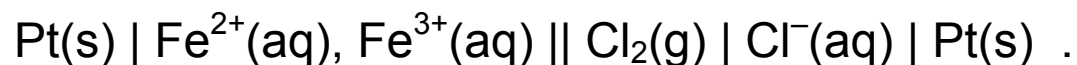
(c) Iron II ions lose electrons to form iron III, while chlorine molecules gain electrons and form chloride ions. The half reactions are



and



An inactive anode and cathode are required – use Pt(s). The cell diagram is



Standard Cell Potential

A voltmeter measures the electric potential difference between the anode and cathode - the *cell potential*, E_{cell} .

The unit of electric potential (i.e., voltage) is the volt: $1 \text{ V} = 1 \text{ J C}^{-1}$ where C is the SI unit of charge – the Coulomb.

The cell potential measured under **standard conditions**, at 25°C, is the *standard cell potential*, E_{cell}° .

For example,

$$E_{\text{cell}}^{\circ}(\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}) = 1.10 \text{ V} .$$

Electrons flows from Zn to Cu^{2+} , through a wire, because there is a chemical driving force.

A chemical driving force is a negative Gibbs free energy of reaction.

The electrostatic potential energy of the transferred electrons drops upon passage from anode to cathode.

When 1 mol of Cu^{2+} reacts with 1 mol of Zn, 2 mol of e^- are transferred. The charge on two moles of electrons is

$$2 \text{ mol} \times (-F) = 2 \text{ mol} \times (-96485 \text{ C mol}^{-1}) = -192970 \text{ C} ,$$

where F is the Faraday constant. It equals the magnitude of charge per mole of electrons. The magnitude of the charge on one mole of electrons is

$$1 \text{ mol} \times F = 1 \text{ mol} \times 96485 \text{ C mol}^{-1} = 96485 \text{ C}$$

The drop in electrostatic potential energy of the transferred electrons is

$$-2 F E_{\text{cell}} = \Delta G$$

$-\Delta G$ = the maximum electrical work that can be done by an electrochemical cell
for 1 mol extent of reaction

In general,

$$-n F E_{\text{cell}} = \Delta G$$

where n is the number of electrons transferred in the balanced cell reaction.

Under *standard conditions* (1 mol L⁻¹ concentration of aqueous species and 1 bar partial pressure of gases),

$$\Delta G^{\circ} = -n F E_{\text{cell}}^{\circ}$$

Positive cell potential corresponds to negative Gibbs free energy of reaction – i.e., the redox reaction is spontaneous.

If the cell potential were negative, the cell runs in the reverse direction – swap the anode and cathode. The cell has positive potential – by definition.

The standard cell potentials for the copper-silver and zinc-silver cells:



Adding the cell reactions for the zinc-copper and copper-silver cells gives the cell reaction for the zinc-silver cell.

Adding the zinc-copper and copper-silver cell potentials gives the cell potential for the zinc-silver cell:

$$\begin{aligned} E_{\text{cell}}^\circ(\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}) &= E_{\text{cell}}^\circ(\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}) \\ &\quad + E_{\text{cell}}^\circ(\text{Cu} \mid \text{Cu}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}) \\ &= 1.10 + 0.46 \text{ V} = 1.56 \text{ V} \end{aligned}$$

Oxidation and Reduction Half-Cell Potential

Every cell reaction is the sum of an oxidation half reaction and a reduction half reaction – or,

the difference between two reduction half reactions.

Cell potential is the sum of an *oxidation half cell potential* and a *reduction half cell potential* – or,

the difference between two reduction half cell potentials.

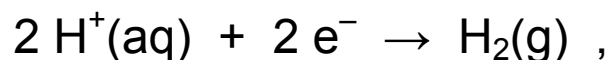
For example,

$$\begin{aligned} E_{\text{cell}}^{\circ}(\text{Zn} | \text{Zn}^{2+} || \text{Ag}^{+} | \text{Ag}) &= E_{\text{ox}}^{\circ}(\text{Zn} | \text{Zn}^{2+}) + E_{\text{red}}^{\circ}(\text{Ag}^{+} | \text{Ag}) \\ &= E^{\circ}[\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-}] + E^{\circ}[\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Ag}(\text{s})] \\ &= E^{\circ}[\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Ag}(\text{s})] - E^{\circ}[\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightarrow \text{Zn}(\text{s})] \\ &= E_{\text{red}}^{\circ}(\text{Ag}^{+} | \text{Ag}) - E_{\text{red}}^{\circ}(\text{Zn}^{2+} | \text{Zn}) \end{aligned}$$

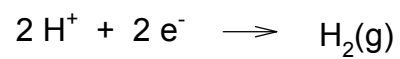
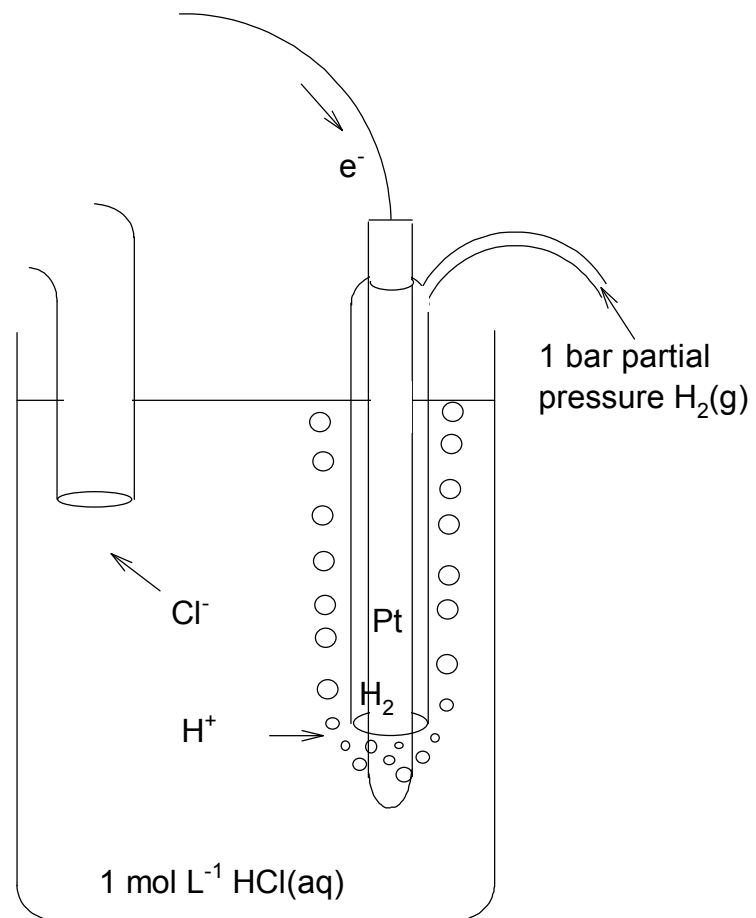
E_{red}° is *standard* reduction half-cell potential, and E_{ox}° is *standard* oxidation half-cell potential.

Note: $E^{\circ}[\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Ag}(\text{s})]$ and $E^{\circ}[\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-}]$ are combined directly, even though the two reduction half-reactions are written with different numbers of electrons.

The *standard reference electrode* is chosen to be the hydrogen electrode – the reduction half cell with half reaction,



under standard conditions ($1 \text{ mol L}^{-1} \text{H}^{+}$ and 1 bar partial pressure of H_2).



The standard reduction potential is defined to be zero.

By setting (this is a convention)

$$E_{\text{red}}^{\circ}(\text{H}^{+} | \text{H}_2) = E^{\circ}[2 \text{H}^{+}(\text{aq}) + 2 \text{e}^{-} \rightarrow \text{H}_2(\text{g})] = 0 \text{ V} ,$$

we can determine all other reduction potentials.

For example,

$$\begin{aligned} E_{\text{red}}^{\circ}(\text{Cu}^{2+} | \text{Cu}) &= E_{\text{red}}^{\circ}(\text{Cu}^{2+} | \text{Cu}) - E_{\text{red}}^{\circ}(\text{H}^{+} | \text{H}_2) \\ &= E_{\text{cell}}^{\circ}(\text{H}_2 | \text{H}^{+} || \text{Cu}^{2+} | \text{Cu}) = 0.34 \text{ V} \end{aligned}$$

Also, the reduction potential for silver is determined from

$$E_{\text{cell}}^{\circ}(\text{Cu} | \text{Cu}^{2+} || \text{Ag}^{+} | \text{Ag}) = 0.46 \text{ V}$$

Since

$$E_{\text{cell}}^{\circ}(\text{Cu} | \text{Cu}^{2+} || \text{Ag}^{+} | \text{Ag}) = E_{\text{red}}^{\circ}(\text{Ag}^{+} | \text{Ag}) - E_{\text{red}}^{\circ}(\text{Cu}^{2+} | \text{Cu}) ,$$

$$E_{\text{red}}^{\circ}(\text{Ag}^{+} | \text{Ag}) = E_{\text{cell}}^{\circ}(\text{Cu} | \text{Cu}^{2+} || \text{Ag}^{+} | \text{Ag}) + E_{\text{red}}^{\circ}(\text{Cu}^{2+} | \text{Cu}) = 0.46 + 0.34 \text{ V}$$

$$= 0.80 \text{ V}$$

Similarly, since

$$E_{\text{cell}}^{\circ}(\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}) = 1.10 \text{ V}$$

$$= E_{\text{red}}^{\circ}(\text{Cu}^{2+} | \text{Cu}) - E_{\text{red}}^{\circ}(\text{Zn}^{2+} | \text{Zn}) = 0.34 \text{ V} - E_{\text{red}}^{\circ}(\text{Zn}) ,$$

we must have

$$E_{\text{red}}^{\circ}(\text{Zn}^{2+} | \text{Zn}) = 0.34 - 1.10 \text{ V} = -0.76 \text{ V} .$$

In general,

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cat}) + E_{\text{ox}}^{\circ}(\text{an})$$

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cat}) - E_{\text{red}}^{\circ}(\text{an})$$

Some standard reduction potentials at 25°C

This data comes from
the Handbook of
Chemistry and Physics.

Reduction half reaction	E_{red}° (V)
$\text{F}_2(\text{g}) + 2\text{e}^{-} \rightarrow 2\text{F}^{-}(\text{aq})$	+2.87
$\text{O}_3(\text{g}) + 2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+2.08
$\text{Co}^{3+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Co}^{2+}(\text{aq})$	+1.92
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightarrow 2\text{H}_2\text{O}(\text{l})$	+1.78
$\text{Ce}^{4+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.72
$\text{PbO}_2(\text{s}) + 4\text{H}^{+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	+1.69
$\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) + 5\text{e}^{-} \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^{-} \rightarrow \text{Au}(\text{s})$	+1.50
$\text{HOCl}(\text{aq}) + \text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cl}^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+1.48
$\text{ClO}_3^{-}(\text{aq}) + 6\text{H}^{+}(\text{aq}) + 6\text{e}^{-} \rightarrow \text{Cl}^{-}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$	+1.45
$\text{Cl}_2(\text{g}) + 2\text{e}^{-} \rightarrow 2\text{Cl}^{-}(\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^{+}(\text{aq}) + 6\text{e}^{-} \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.36

$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$	+1.23
$\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	+1.22
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2 \text{Br}^-(\text{aq})$	+1.07
$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	+0.96
$2 \text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}(\text{aq})$	+0.92
$\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 2 \text{OH}^-(\text{aq})$	+0.81
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow 2 \text{Hg}(\text{l})$	+0.80
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.70
$\text{MnO}_4^-(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 3\text{e}^- \rightarrow \text{MnO}_2(\text{s}) + 4 \text{OH}^-(\text{aq})$	+0.60
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2 \text{I}^-(\text{aq})$	+0.54
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4 \text{OH}^-(\text{aq})$	+0.40
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
$\text{SO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{SO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	+0.20

$\text{Cu}^{2+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Cu}^{+}(\text{aq})$	+0.15
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.15
$2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{H}_2(\text{g})$	0
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Ni}(\text{s})$	-0.26
$\text{PbSO}_4(\text{s}) + 2\text{e}^{-} \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.36
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Fe}(\text{s})$	-0.45
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^{-} \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^{-} \rightarrow \text{H}_2(\text{g}) + \text{OH}^{-}(\text{aq})$	-0.83
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^{-} \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Sr}(\text{s})$	-2.90
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Ba}(\text{s})$	-2.91
$\text{K}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{K}(\text{s})$	-2.93
$\text{Li}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Li}(\text{s})$	-3.04

Example: Use the Table to determine the standard cell potential at 25°C for cells with the following cell diagrams.

- (a) $\text{Zn(s)} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Ni}^{2+}(\text{aq}) \mid \text{Ni(s)}$
- (b) $\text{Sn(s)} \mid \text{Sn}^{2+}(\text{aq}) \parallel \text{Fe}^{3+}(\text{aq}), \text{Fe}^{2+}(\text{aq}) \mid \text{Pt(s)}$
- (c) $\text{Pt(s)} \mid \text{I}^{-}(\text{aq}) \mid \text{I}_2(\text{s}) \parallel \text{NO}_3^{-}(\text{aq}), \text{H}^{+}(\text{aq}) \mid \text{NO(g)} \mid \text{Pt(s)}$
- (d) $\text{Li(s)} \mid \text{Li}^{+}(\text{aq}) \parallel \text{F}_2(\text{g}) \mid \text{F}^{-}(\text{aq}) \mid \text{Pt(s)}$

(a) The half reactions are



and



The associated standard reduction potentials are -0.25 V for the reduction of $\text{Ni}^{2+}(\text{aq})$ and -0.76 V for the reduction of $\text{Zn}^{2+}(\text{aq})$ (the reverse of the oxidation half reaction). Therefore,

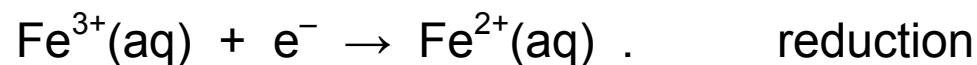
$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{Ni}^{2+} \mid \text{Ni}) - E_{\text{red}}^{\circ}(\text{Zn}^{2+} \mid \text{Zn})$$

$$= -0.26 - (-0.76) \text{ V} = +0.50 \text{ V} .$$

(b) The half reactions are



and



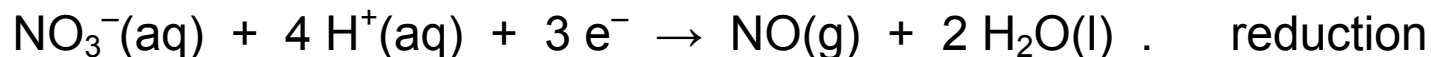
The cell potential is

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}(\text{Fe}^{3+} | \text{Fe}^{2+}) - E_{\text{red}}^{\circ}(\text{Sn}^{2+} | \text{Sn}) \\ &= +0.77 - (-0.14) \text{ V} = +0.91 \text{ V} . \end{aligned}$$

(c) The half reactions are



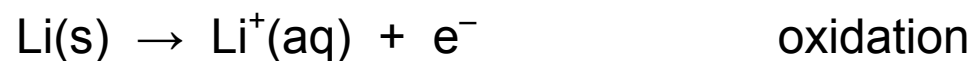
and



The cell potential is

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}(\text{NO}_3^- | \text{NO}) - E_{\text{red}}^{\circ}(\text{I}_2 | \text{I}^-) \\ &= +0.96 - 0.54 \text{ V} = +0.42 \text{ V} . \end{aligned}$$

(d) The half reactions are



and



The cell potential is

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}(\text{F}_2 | \text{F}^-) - E_{\text{red}}^{\circ}(\text{Li}^+ | \text{Li}) \\ &= +2.87 - (-3.04) \text{ V} = +5.91 \text{ V} . \end{aligned}$$

The **reactant**, in a reduction half reaction, is an **oxidizing** agent.

The **strongest** oxidizing agent, fluorine gas, appears at the **top** of the table.

Oxidizing agents are ordered (increasing in strength) from **bottom to top** in the table.

The **product**, in a reduction half reaction, is a **reducing** agent.

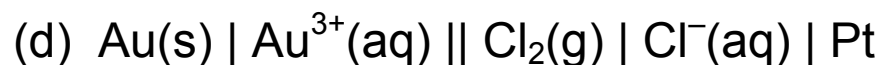
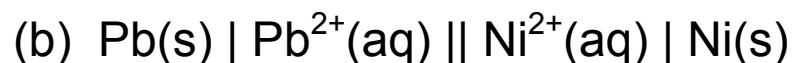
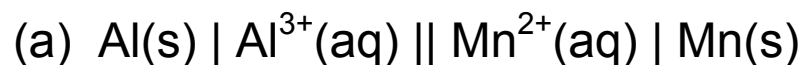
The **strongest** reducing agent, lithium metal, appears at the **bottom** of the table.

Reducing agents are ordered from **top to bottom** in the table.

Each oxidizing agent oxidizes any reducing agent from a **lower** row in the table.

Such a combination produces a cell with a **spontaneous** cell reaction and **positive** cell potential.

Example: Which of the following cell diagrams have a spontaneous cell reaction, under standard conditions? For those that do not, re-write the cell diagram to have a spontaneous cell reaction. For each cell, identify the anode and cathode, and the oxidizing and reducing agents, when the cell runs in the spontaneous direction.



(a) The reduction potential of $\text{Mn}^{2+}(\text{aq})$ is above that of $\text{Al}^{3+}(\text{aq})$; -1.19 V versus -1.66 V , respectively. Therefore, the cell potential is positive, and the cell diagram is written in the correct spontaneous direction. Aluminum is the anode, and manganese is the cathode. Aluminum is the reducing agent, and manganese II is the oxidizing agent.

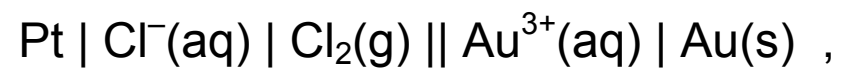
(b) The reduction potential of $\text{Pb}^{2+}(\text{aq})$ is above that of $\text{Ni}^{2+}(\text{aq})$; -0.13 V versus -0.26 V , respectively. Therefore, the cell potential is negative, and the cell diagram is written in the non-spontaneous direction. The cell diagram is re-written as



to make the cell potential positive. Nickel is the anode, and lead is the cathode. Nickel is the reducing agent, and lead II is the oxidizing agent.

(c) The reduction potential of $\text{Sn}^{4+}(\text{aq})$ is above that of $\text{H}^{+}(\text{aq})$; $+0.15 \text{ V}$ versus 0 V , respectively. Therefore, the cell potential is positive, and the cell diagram is written in the correct spontaneous direction. The anode and cathode are both inactive, and consist of platinum. Hydrogen is the reducing agent, and tin IV is the oxidizing agent.

(d) The reduction potential of $\text{Au}^{3+}(\text{aq})$ is above that of $\text{Cl}_2(\text{g})$; $+1.50 \text{ V}$ versus $+1.36 \text{ V}$, respectively. Therefore, the cell potential is negative, and the cell diagram is written in the non-spontaneous direction. The cell diagram is re-written as



to make the cell potential positive. Platinum is the anode, and gold is the cathode. Chloride is the reducing agent, and gold III is the oxidizing agent.

Cell Potential and Equilibrium

$$-R T \ln K = \Delta G^{\circ} = -n F E_{\text{cell}}^{\circ}$$

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

$$K = \exp\left(\frac{nFE_{\text{cell}}^{\circ}}{RT}\right)$$

Positive cell potential corresponds to negative Gibbs free energy of reaction, and equilibrium constant greater than one – i.e., a favorable forward reaction.

Non-standard Conditions and the Nernst Equation

$$-n F E_{\text{cell}} = -n F E_{\text{cell}}^{\circ} + R T \ln Q ,$$

or

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

The *Nernst equation*

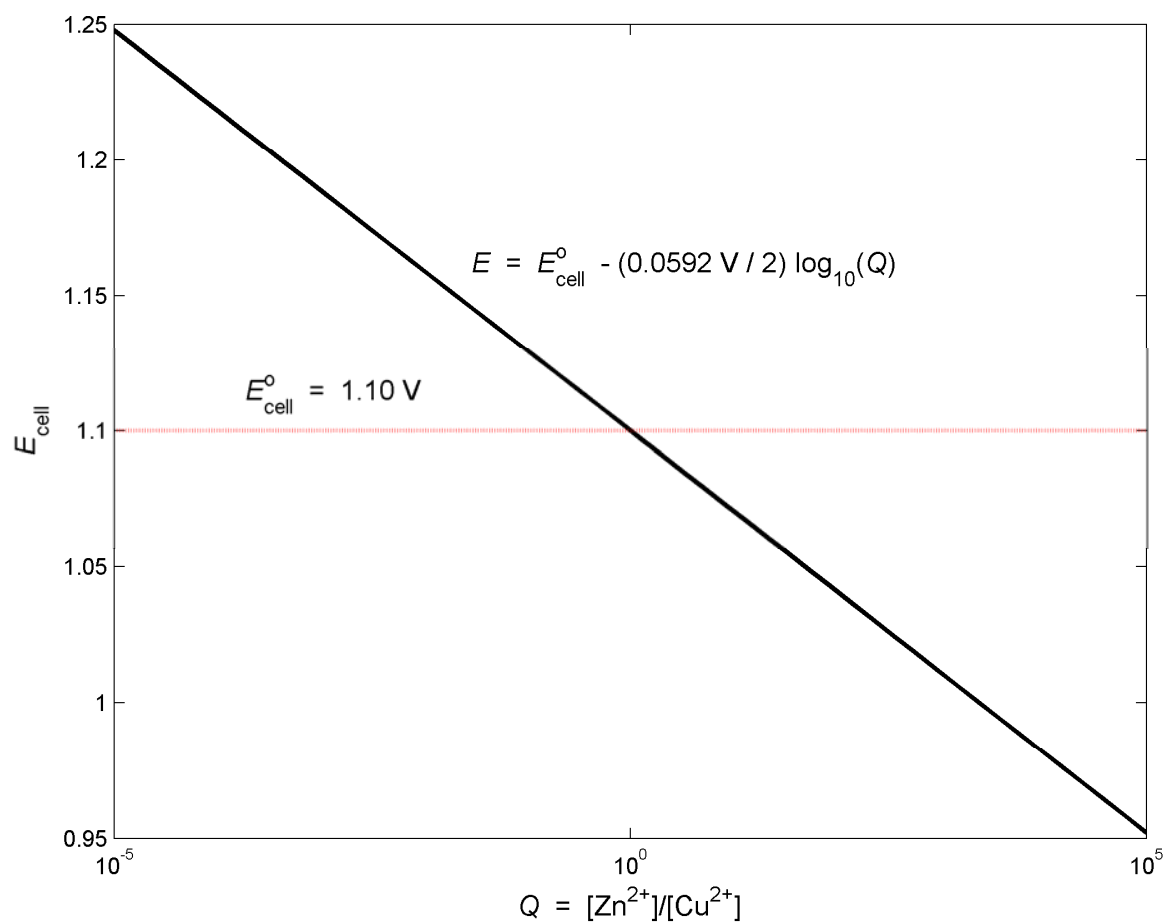
At $T = 298.15 \text{ K}$ (25°C),

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q$$

In terms of the base 10 logarithm,

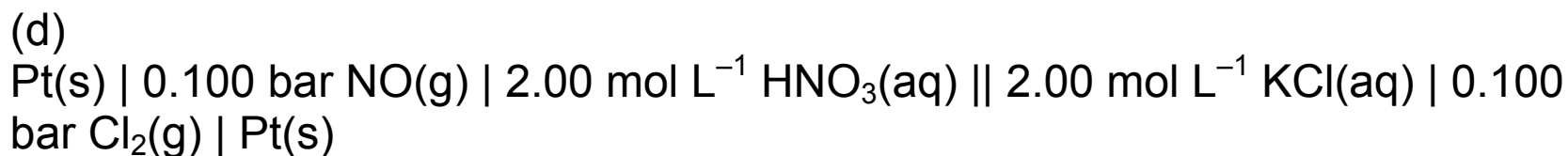
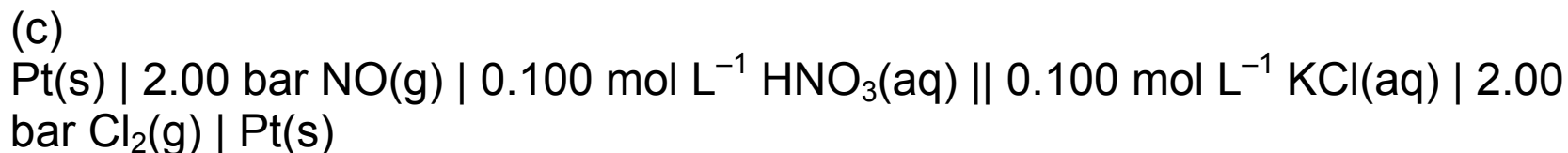
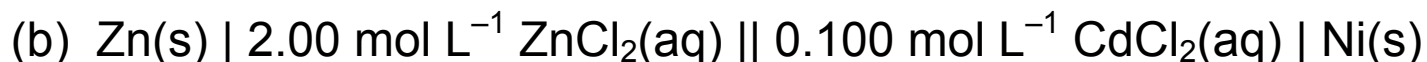
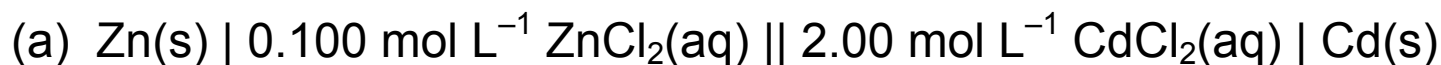
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log_{10} Q$$

Significant deviations from the standard cell potential require either a *very small* or *very large* reaction quotient.

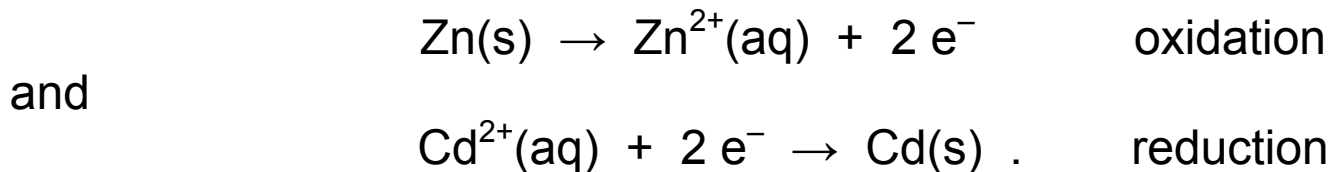


Cell potential for zinc-copper cell versus reaction quotient, $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$.

Example: Determine the cell potentials, at 25°C, for the following cells.



(a) The half reactions are



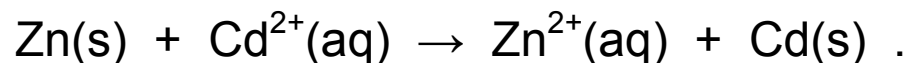
Under standard conditions, the cell potential is

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}(\text{Cd}^{2+} | \text{Cd}) - E_{\text{red}}^{\circ}(\text{Zn}^{2+} | \text{Zn}) \\ &= -0.40 - (-0.76) \text{ V} = +0.36 \text{ V} . \end{aligned}$$

Under the given conditions, the cell potential shifts to

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q$$

We need the reaction quotient, Q . The balanced cell reaction is (with $n = 2$ electrons transferred)



Therefore,

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]} = \frac{0.100}{2.00} = 0.0500$$

and

$$E_{\text{cell}} = 0.36 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln(0.0500) \\ = 0.40 \text{ V} .$$

Depleted product ($\text{Zn}^{2+}(\text{aq})$) and excess reactant ($\text{Cd}^{2+}(\text{aq})$), compared to standard conditions, yield a larger than standard cell potential.

(b) This is the same cell as in part (a), except the non-standard conditions are different. Here,

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]} = \frac{2.00}{0.100} = 20.0$$

and

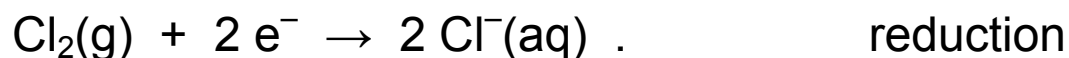
$$E_{\text{cell}} = 0.36 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln(20.0) \\ = 0.32 \text{ V} .$$

Excess product ($\text{Zn}^{2+}(\text{aq})$) and depleted reactant ($\text{Cd}^{2+}(\text{aq})$), compared to standard conditions, yield a lower than standard cell potential.

(c) The half reactions are



and



Under standard conditions, the cell potential is

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}(\text{Cl}_2 | \text{Cl}^-) - E_{\text{red}}^{\circ}(\text{NO}_3^- | \text{NO}) \\ &= +1.36 - (+0.96) \text{ V} = +0.40 \text{ V} . \end{aligned}$$

Under the given conditions, the cell potential shift to

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q$$

The balanced cell reaction is (with $n = 6$ electrons transferred)



Therefore,

$$Q = \frac{[\text{Cl}^-]^6 [\text{NO}_3^-]^2 [\text{H}^+]^8}{P_{\text{Cl}_2}^3 P_{\text{NO}}^2}$$
$$= \frac{0.100^6 \times 0.100^2 \times 0.100^8}{2.00^3 \times 2.00^2} = 3.12_5 \times 10^{-18}$$

and

$$E_{\text{cell}} = 0.40 \text{ V} - \frac{0.0257 \text{ V}}{6} \ln(3.12_5 \times 10^{-18})$$
$$= 0.57 \text{ V} .$$

Depleted products ($\text{Cl}^-(\text{aq})$, $\text{NO}_3^-(\text{aq})$ and $\text{H}^+(\text{aq})$) and excess reactants ($\text{Cl}_2(\text{g})$ and $\text{NO}(\text{g})$), compared to standard conditions, yield a larger than standard cell potential.

(d) This is the same cell as in part (c), except the non-standard conditions are different. Here,

$$Q = \frac{[\text{Cl}^-]^6 [\text{NO}_3^-]^2 [\text{H}^+]^8}{P_{\text{Cl}_2}^3 P_{\text{NO}}^2}$$

$$= \frac{2.00^6 \times 2.00^2 \times 2.00^8}{0.100^3 \times 0.100^2} = 6.55_4 \times 10^9$$

and

$$E_{\text{cell}} = 0.40 \text{ V} - \frac{0.0257 \text{ V}}{6} \ln(6.55_4 \times 10^9)$$

$$= 0.30 \text{ V} .$$

Measuring Concentrations with Electrochemical Cells

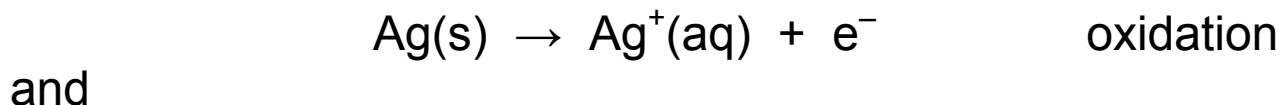
Example: Determine the molar solubility of silver bromide, at 25°C, given the following electrochemical cell potential, and data from Table of standard reduction potentials.

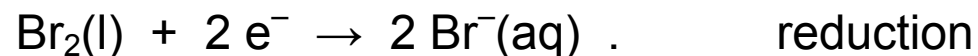


AgBr(aq, sat) is a saturated solution of silver bromide – it is prepared by dissolving silver bromide in water until no more silver bromide dissolves – i.e., undissolved solid silver bromide remains in anode half cell at equilibrium.

Note that there is bromide in both the cathode and anode half cells. However, only the bromide in the cathode half cell is active.

The half reactions are





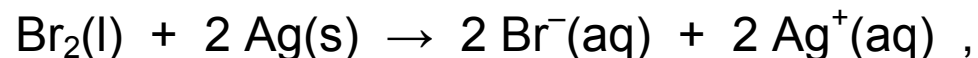
Under standard conditions, the cell potential is

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}(\text{Br}_2 | \text{Br}^-) - E_{\text{red}}^{\circ}(\text{Ag}^+ | \text{Ag}) \\ &= 1.07 - (0.80) \text{ V} = 0.27 \text{ V} \end{aligned}$$

Under the given conditions, the cell potential shifts to

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q \\ 0.69 \text{ V} &= 0.27 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln Q , \\ Q &= \exp\left(\frac{2 \times (-0.42)}{0.0257}\right) = 6.3_9 \times 10^{-15} . \end{aligned}$$

The balanced cell reaction is (with $n = 2$ electrons transferred)



where $\text{Br}^-(\text{aq})$ refers to bromide concentration in the cathode half cell – not the spectator bromide concentration in the anode half cell. Therefore,

$$\begin{aligned} Q &= [\text{Br}^-]^2 [\text{Ag}^+]^2 \\ &= 0.100^2 [\text{Ag}^+]^2 = 6.3_9 \times 10^{-15} , \end{aligned}$$

or

$$[\text{Ag}^+] = \sqrt{\frac{6.3_9 \times 10^{-15}}{0.100^2}} = 8.0 \times 10^{-7} \text{ mol L}^{-1} .$$

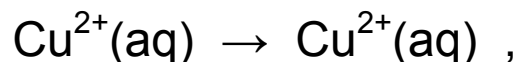
The molar solubility of silver bromide is the concentration of Ag^+ or Br^- in the saturated silver bromide solution in the anode half cell –
it is $8.0 \times 10^{-7} \text{ mol L}^{-1}$.

Concentration Cells

Consider



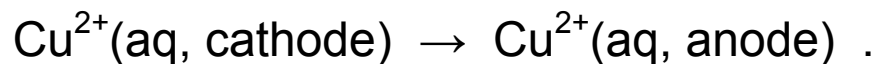
The associated net the ionic equation is



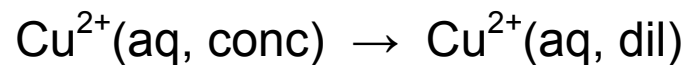
and the standard cell potential is

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{Cu}^{2+} \mid \text{Cu}) - E_{\text{red}}^{\circ}(\text{Cu}^{2+} \mid \text{Cu}) = 0 \text{ V}$$

Consider non-standard conditions:



This reaction is spontaneous – with positive cell potential – if the concentration is higher at the cathode:



The natural direction of flow of copper II ions.

At 25°C, the cell potential is

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q \\ &= -\frac{0.0257 \text{ V}}{2} \ln \left(\frac{[\text{Cu}^{2+}, \text{anode}]}{[\text{Cu}^{2+}, \text{cathode}]} \right) \\ &= -\frac{0.0257 \text{ V}}{2} \ln \left(\frac{[\text{Cu}^{2+}, \text{dil}]}{[\text{Cu}^{2+}, \text{conc}]} \right) > 0 . \end{aligned}$$

Example: Determine the cell potential for the copper II concentration cell described above given $[\text{Cu}^{2+}, \text{cathode}] = 1.00 \text{ mol L}^{-1}$ and (a) $[\text{Cu}^{2+}, \text{anode}] = 0.100 \text{ mol L}^{-1}$, (b) $[\text{Cu}^{2+}, \text{anode}] = 0.0100 \text{ mol L}^{-1}$, and (c) $[\text{Cu}^{2+}, \text{anode}] = 0.00100 \text{ mol L}^{-1}$.

(a)

$$\begin{aligned} E_{\text{cell}} &= -\frac{0.0592 \text{ V}}{2} \log_{10} \left(\frac{[\text{Cu}^{2+}, \text{anode}]}{[\text{Cu}^{2+}, \text{cathode}]} \right) \\ &= -0.0296 \text{ V} \times \log_{10} \left(\frac{[\text{Cu}^{2+}, \text{dil}]}{[\text{Cu}^{2+}, \text{conc}]} \right) \\ &= 0.0296 \text{ V} \times \log_{10} \left(\frac{1.00}{0.100} \right) = 0.0296 \text{ V}. \end{aligned}$$

(b)

$$E_{\text{cell}} = 0.0296 \text{ V} \times \log_{10} \left(\frac{1.00}{0.0100} \right) = 0.0592 \text{ V}.$$

(c)

$$E_{\text{cell}} = 0.0296 \text{ V} \times \log_{10} \left(\frac{1.00}{0.00100} \right) = 0.0888 \text{ V}.$$

The pH Meter

A *pH meter* measures the concentration of hydrogen ions. It is a concentration cell.

The *glass membrane electrode* contains an HCl solution with an accurately determined concentration (e.g., 1.000 mol L⁻¹), and a silver electrode coated with a thin layer of solid silver chloride.

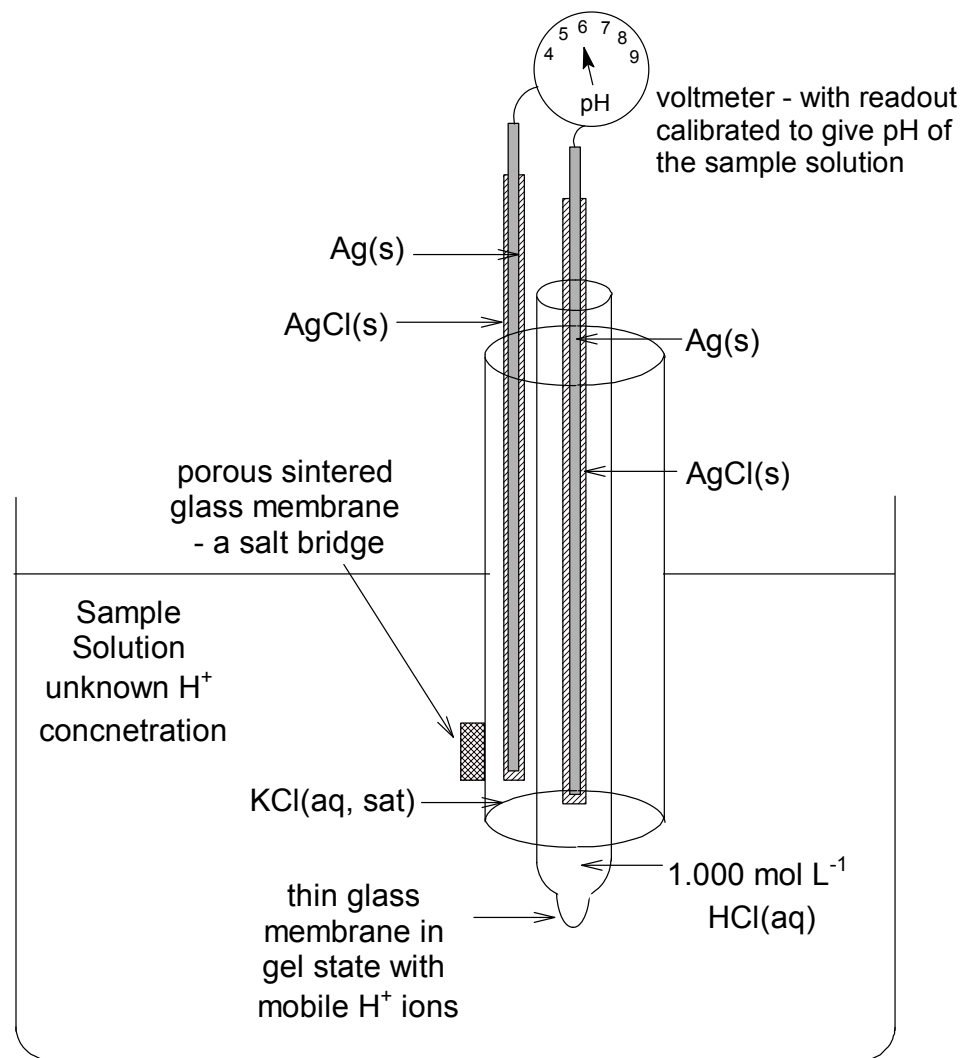
At the end of the tube, the glass is very thin, and in a gel state – a hydrated state of glass – with hydrogen ions within the glass.

Hydrogen ions can flow across the glass here, and carry a current.

A pH meter constructed from two silver-silver chloride half cells within concentric glass tubes.

The inner half cell is the glass membrane electrode.

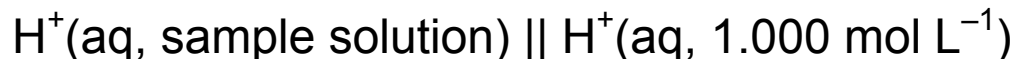
The outer half cell is connected to the sample solution by a porous sintered glass membrane that provides a salt bridge.



The cell diagram for the above pH meter is



except that *imbedded* within this cell (after the salt bridge) is a *hydrogen ion concentration cell*,



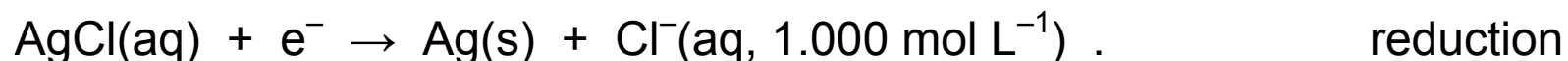
The hydrogen ion concentration cell is in series with the silver-silver chloride cell, since current must pass through it (i.e., across the glass membrane) in order to complete the circuit.

The potential of the hydrogen ion concentration adds to the potential of the silver-silver chloride cell.

For the silver-silver chloride cell, the half reactions are



and



Therefore, $n = 1$ for this cell, and the cell reaction is

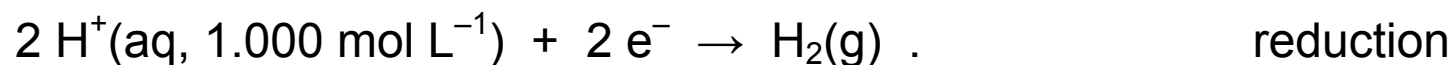


The silver-silver chloride cell is itself a chloride concentration cell. However, the chloride concentrations are fixed. This cell provides a reference potential, and ensures a good electrical connection.

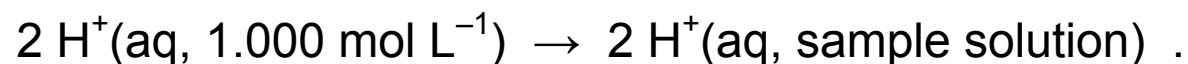
For the hydrogen concentration cell, the half reactions are



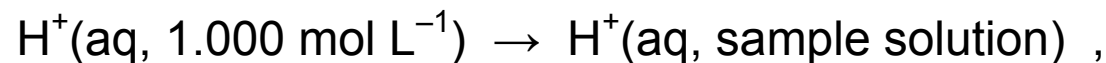
and



Therefore, $n = 2$ for this cell, and the cell reaction is



The factor of two on both sides of the equation can be canceled to give cell reaction,



for which $n = 1$.

Applying the Nernst equation to both cells and adding the result gives

$$\begin{aligned} E_{\text{total}} &= -\frac{0.0592 \text{ V}}{1} \log_{10} \left(\frac{[\text{Cl}^-, 1.000 \text{ mol L}^{-1}]}{[\text{Cl}^-, \text{saturated KCl solution}]} \right) - 0.0592 \text{ V} \times \log_{10} \left(\frac{[\text{H}^+, \text{sample solution}]}{[\text{H}^+, 1.000 \text{ mol L}^{-1}]} \right) \\ &= E_{\text{ref}} - 0.0592 \text{ V} \times \log_{10} ([\text{H}^+, \text{sample solution}]) \\ &= E_{\text{ref}} + 0.0592 \text{ V} \times \text{pH} . \end{aligned}$$

Here, E_{ref} is accurately known. It corresponds to the measured cell potential when $\text{pH} = 0$.

The measured potential increases by 0.0592 V for each unit of pH.

Concentration Cells in Living Systems

Mitochondria store energy in a hydrogen ion concentration gradient.

This energy storing process is called the *electron transport chain*.

The energy released by the discharge of this concentration cell is used to produce ATP for distribution throughout the cell.

Concentration cells are central to signal transmission through nerve and muscle cells.

These cells have sodium, potassium, chloride and calcium concentration differences across their outer membranes.

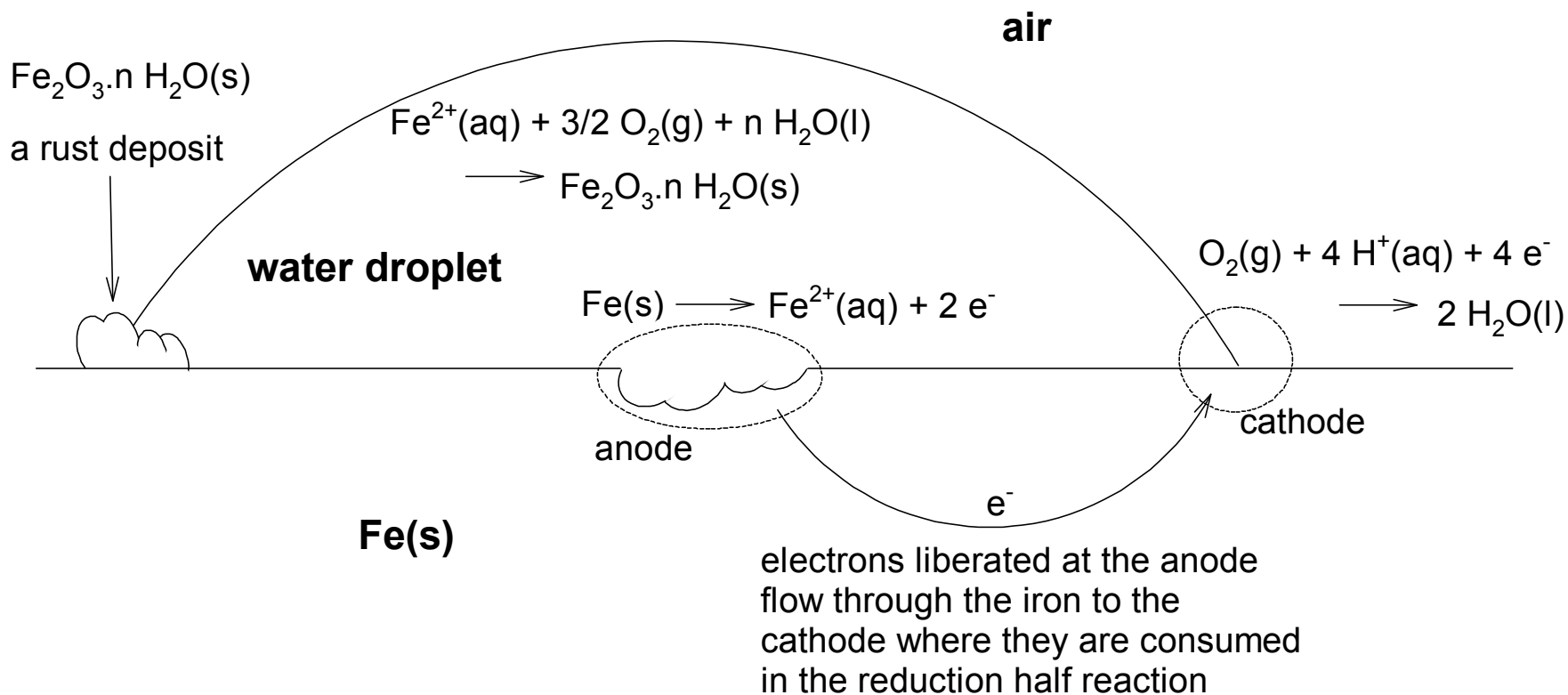
Corrosion

The oxidation of iron (steel) by atmospheric oxygen to form iron oxide (rust) is spontaneous.

Very slow under dry conditions.

Much faster under wet conditions – especially acidic and/or salty wet conditions.

Steel must be protected with paints (e.g., in the case of cars), or cathodic protection (e.g., on ships).



Acid rain accelerates corrosion – H^{+} is a reactant in the reduction half reaction.

Salt in solution accelerates corrosion – it facilitates better electrical conductivity to complete the circuit outside the metal.

Iron can be protected from corrosion by paints which prevent water and air from contacting the iron surface.

Corrosion is also prevented by *cathodic protection*. The metal to be protected is coated with a *more active metal* – i.e., a metal with a lower reduction potential.

For example, iron is typically coated with zinc for this purpose. This coating process is called *galvanization*. The result is galvanized steel.

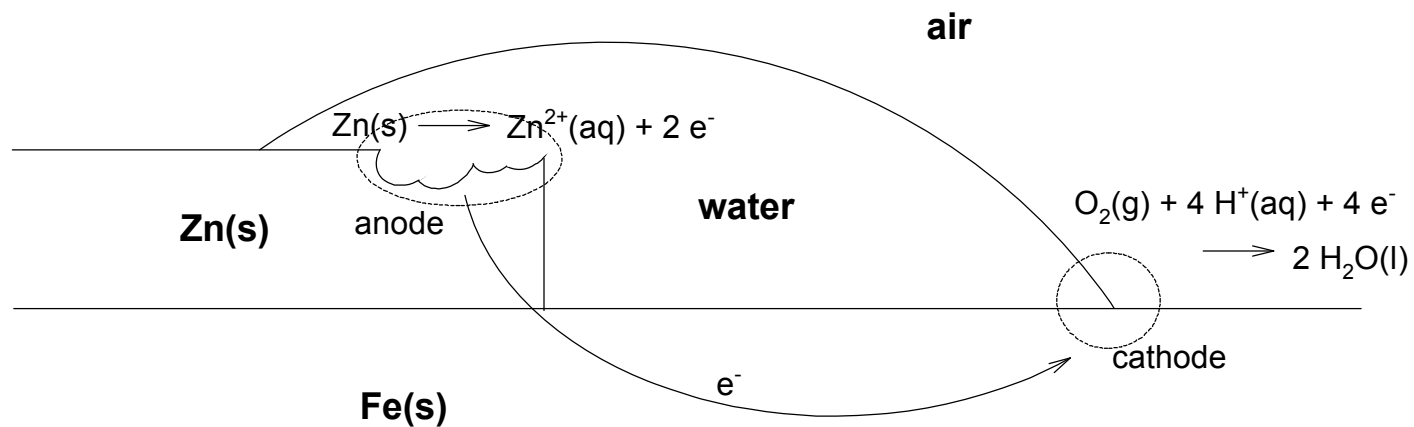
The more active metal is always corroded first.

Ships are protected with a large block of zinc attached to the hull and submerged in the water to make a complete circuit.

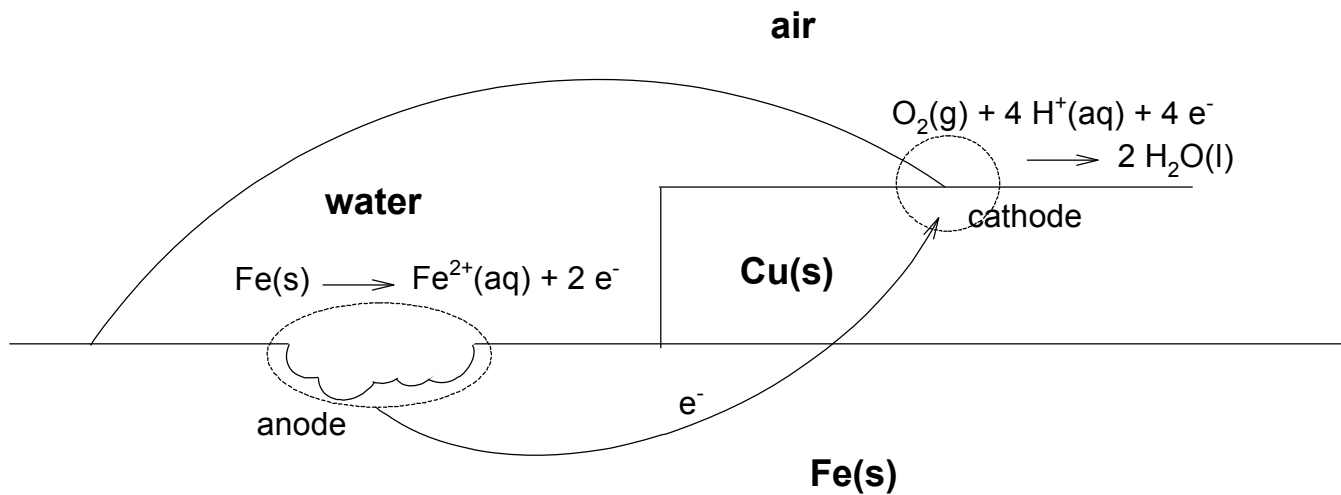
If iron were coated with a less active metal (i.e., it has a higher reduction potential), such as copper, then it is not protected. In fact, the attached copper makes the iron more susceptible to corrosion.

Copper, or any other less active metal than iron, provides a better cathode material for the reduction of oxygen.

Cathodic protection of iron with zinc



Enhanced corrosion of iron with copper



Example: Consider the following list of metals: Al, Mg, Sr, Cr, Zn, Cd, Ni, Fe, Cu, Pb and Ag. Which of these metals are suitable to use as cathodic protection for (a) iron, (b) copper, and (c) zinc?

The reduction potentials have the following order:

$\text{Ag} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cd} > \text{Fe} > \text{Cr} > \text{Zn} > \text{Al} > \text{Mg} > \text{Sr}$

(a) Cr, Zn, Al, Mg and Sr have lower reduction potentials than Fe, and can therefore be used as cathodic protection agents. Since strontium reacts with water, it would never be used as a cathodic protection agent in any normal application.

(b) Pb, Ni, Cd, Fe, Cr, Zn, Al, Mg and Sr have lower reduction potentials than Cu, and can therefore be used as cathodic protection agents (with the above caveat regarding strontium).

(c) Al, Mg and Sr have lower reduction potentials than Zn, and can therefore be used as cathodic protection agents (with the above caveat regarding strontium).

Batteries

Primary (cheaper, resist discharging when not used) and secondary (rechargeable) cells.

Attempts to recharge primary cells result in side reactions.

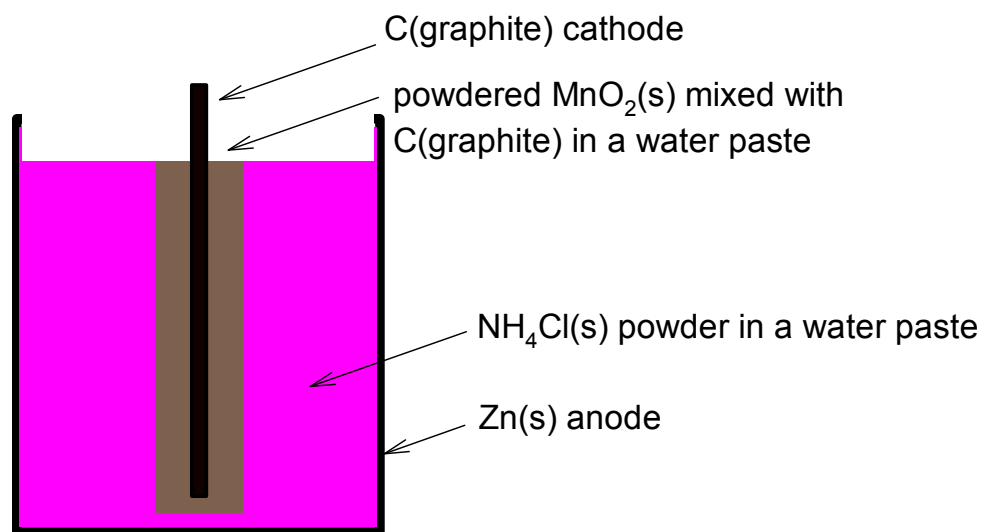
Reactants are incompletely replenished.

Irreversible changes occur, including the production of gases such as ammonia (in an NH_4Cl dry cell) or hydrogen.

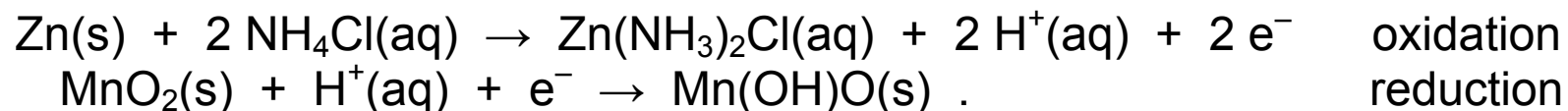
Hydrogen gas pressure buildup within the battery can lead to battery explosion. In any case, primary batteries do not perform well after recharging.

The dry cell – Leclanché cell – and the alkaline cell are two common primary cells based on zinc (the reducing agent) and manganese dioxide (the oxidizing agent).

The dry cell – Leclanché cell



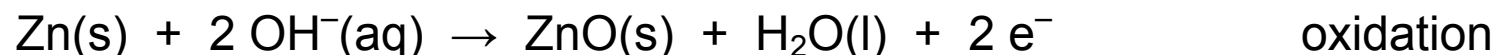
Half reactions:



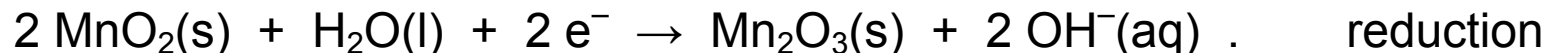
Reduction of $\text{H}^+(\text{aq})$ can occur at the cathode (or the anode if one is attempting to recharge a dry cell), to form hydrogen gas which reduces power output (by increasing internal resistance) and can be dangerous.

The *alkaline cell* has a much lower H^+ concentration.

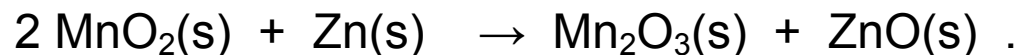
Half reactions:



and



The net cell reaction for the alkaline cell is



The important secondary cells are nickel-cadmium, lithium and lead-acid batteries.

Like the alkaline cell, the nickel-cadmium and lithium cells have net cell reactions with solid reactants and products. These provide a constant voltage during discharge.

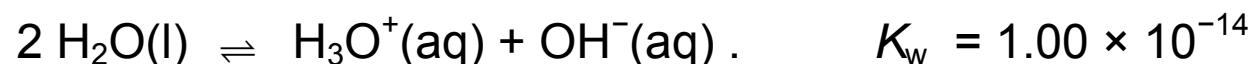
The lead acid cell consumes $\text{H}^+(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$, and its potential depends on extent of reaction. However, the lead-acid battery in a car is continually recharged as the car runs.

Fuel cells are cells with reactants continuously fed into the cell, while products are removed.

The hydrogen fuel cell uses hydrogen gas as the reducing agent at the anode and oxygen gas (from the atmosphere) at the cathode.

Acid-base Equilibrium

Autoionization of Water



In pure water, equilibrium concentrations of hydronium and hydroxide are determined as follows:

	$2 \text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{H}_3\text{O}^+(\text{aq})$	+	$\text{OH}^-(\text{aq})$
Initial			0		0
Change			+ x		+ x
Equilibrium			x		x

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = x^2 = 1.00 \times 10^{-14}$$

or

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = x = 1.00 \times 10^{-7} \text{ mol L}^{-1}$$

Autoionization imposes the equilibrium condition,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

If one of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ is known, the other is determined by the above equation.

For example, in a 1.00 mol L^{-1} HCl solution,

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14}}{1.00} = 1.00 \times 10^{-14} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10}([\text{H}_3\text{O}^+]) \quad \text{and} \quad \text{pOH} = -\log_{10}([\text{OH}^-])$$

Applying $-\log_{10}$ to equilibrium equation,

$$\begin{aligned} \text{p}K_w &= -\log_{10}(1.00 \times 10^{-14}) = 14.00 \\ &= -\log_{10}([\text{H}_3\text{O}^+]) - \log_{10}([\text{OH}^-]) = \text{pH} + \text{pOH} . \end{aligned}$$

For example, a $5.00 \times 10^{-3} \text{ mol L}^{-1}$ solution of sodium hydroxide has

$$\text{pOH} = -\log_{10}(5.00 \times 10^{-3}) = 2.30$$

and

$$\text{pH} = 14.00 - 2.30 = 11.70 .$$

Acid Dissociation Equilibrium

Strong acids dissociate completely and do not require an equilibrium analysis.

Consider the dissociation of ethanoic acid, a *weak* acid – showing the water and hydronium explicitly.



Initial	1.00	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$1.00 - x$	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{1.00 - x} = 1.8 \times 10^{-5}$$

This equation can be rearranged to quadratic form,

$$x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-5} \times 1.00 = 0$$

with solution,

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 + 4 \times 1.8 \times 10^{-5} \times 1.00}}{2}$$

$$= \begin{cases} 4.2_3 \times 10^{-3} \\ -4.2_5 \times 10^{-3} \end{cases}$$

Only the positive solution is admissible. Therefore, the equilibrium concentrations are

$$[\text{CH}_3\text{COOH}] = 1.00 - x = 0.99_6 \text{ mol L}^{-1} = 1.00 \text{ mol L}^{-1}$$

$$[\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+] = x = 4.2 \times 10^{-3} \text{ mol L}^{-1}$$

The concentration of CH_3COOH changes very little.

An approximate solution results if x is neglected in the denominator of the K_a expression.

Specifically,

$$\frac{x^2}{1.00} = 1.8 \times 10^{-5}$$

$$x = \sqrt{1.8 \times 10^{-5} \times 1.00} = 4.2_4 \times 10^{-3}$$

In general, given an initial weak acid concentration, $[\text{HA}]_{\text{initial}}$, and acid dissociation constant, K_a , the extent of reaction is approximated by

$$x \cong \sqrt{K_a [\text{HA}]_{\text{initial}}}$$

A good approximation if $[\text{HA}]_{\text{initial}} \gg K_a$.

Example: Use the approximation,

$$[\text{HA}]_{\text{eqm}} = [\text{HA}]_{\text{initial}} - x \approx [\text{HA}]_{\text{initial}}$$

to determine the pH of 2.00 mol L^{-1} solutions of

- | | |
|----------------------|-------------------------------|
| (a) HF | $K_a = 6.3 \times 10^{-4}$ |
| (b) HCN | $K_a = 6.2 \times 10^{-10}$ |
| (a) H ₂ S | $K_{a1} = 8.9 \times 10^{-8}$ |

(a)

	HF(aq)	+ H₂O(l)	\rightleftharpoons	F⁻(aq)	+	H₃O⁺(aq)
Initial	2.00			0		0
Change	$-x$			$+x$		$+x$
Equilibrium	$2.00 - x$			x		x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{2.00 - x} = 6.3 \times 10^{-4}$$

$2.00 - x \approx 2.00$, gives

$$\frac{x^2}{2.00} = 6.3 \times 10^{-4}$$

$$x = \sqrt{6.3 \times 10^{-4} \times 2.00} = 3.5_5 \times 10^{-2}$$

Therefore,

$$[\text{H}_3\text{O}^+] = x = 3.5_5 \times 10^{-2} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10}([\text{H}_3\text{O}^+]) = -\log_{10}(3.5_5 \times 10^{-2}) = 1.45$$

(b) Same as part (a) except $K_a = 6.2 \times 10^{-10}$.

The extent of reaction at equilibrium is given by

$$\frac{x^2}{2.00} = 6.2 \times 10^{-10}$$

$$x = \sqrt{6.2 \times 10^{-10} \times 2.00} = 3.5_2 \times 10^{-5}$$

Therefore,

$$[\text{H}_3\text{O}^+] = x = 3.5_2 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10}([\text{H}_3\text{O}^+]) = -\log_{10}(3.5_2 \times 10^{-5}) = 4.45 \text{ .}$$

(c) Here,

$$x = \sqrt{8.9 \times 10^{-8} \times 2.00} = 4.2_2 \times 10^{-4}$$

and

$$[\text{H}_3\text{O}^+] = x = 4.2_2 \times 10^{-4} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10}([\text{H}_3\text{O}^+]) = -\log_{10}(4.2_2 \times 10^{-4}) = 3.37 \text{ .}$$

Example: What is the pH of a $1.00 \times 10^{-3} \text{ mol L}^{-1}$ solution of methanoic acid, HCOOH(aq) ($K_a = 1.8 \times 10^{-4}$)? What is the *percent dissociation* of methanoic acid in this solution – i.e., the percentage of the initial methanoic acid that dissociates?

In this case, the initial HA concentration is less than 6 times bigger than K_a . We must solve the quadratic equation.

	HCOOH(aq)	$+ \text{H}_2\text{O(l)}$	\rightleftharpoons	$\text{HCOO}^-(\text{aq})$	$+ \text{H}_3\text{O}^+(\text{aq})$
Initial	1.00×10^{-3}			0	0
Change	$-x$			$+x$	$+x$
Equilibrium	$1.00 \times 10^{-3} - x$			x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{x^2}{1.00 \times 10^{-3} - x} = 1.8 \times 10^{-4}$$

This equation is rearranged to quadratic form,

$$x^2 + 1.8 \times 10^{-4} x - 1.8 \times 10^{-4} \times 1.00 \times 10^{-3} = 0$$

with solution,

$$x = \frac{-1.8 \times 10^{-4} \pm \sqrt{(1.8 \times 10^{-4})^2 + 4 \times 1.8 \times 10^{-4} \times 1.00 \times 10^{-3}}}{2}$$

$$= \begin{cases} 3.4_4 \times 10^{-4} \\ -5.2_4 \times 10^{-4} \end{cases}$$

Only the positive solution is admissible. Therefore, the extent of dissociation is 3.4×10^{-4} and the equilibrium concentrations are given by

$$\begin{aligned} [\text{HCOOH}] &= 1.00 \times 10^{-3} - x = 1.00 \times 10^{-3} - 3.4 \times 10^{-4} = 6.6 \times 10^{-4} \text{ mol L}^{-1} \\ [\text{HCOO}^-] &= [\text{H}_3\text{O}^+] = x = 3.4 \times 10^{-4} \text{ mol L}^{-1} . \end{aligned}$$

$$\text{pH} = -\log_{10}([\text{H}_3\text{O}^+]) = -\log_{10}(3.4 \times 10^{-4}) = 3.47.$$

The percent dissociation of methanoic acid here is given by

$$100\% \times [\text{HCOO}^-] / [\text{HCOOH}]_{\text{initial}} = 3.4 \times 10^{-4} / 1.00 \times 10^{-3} = 34\% .$$

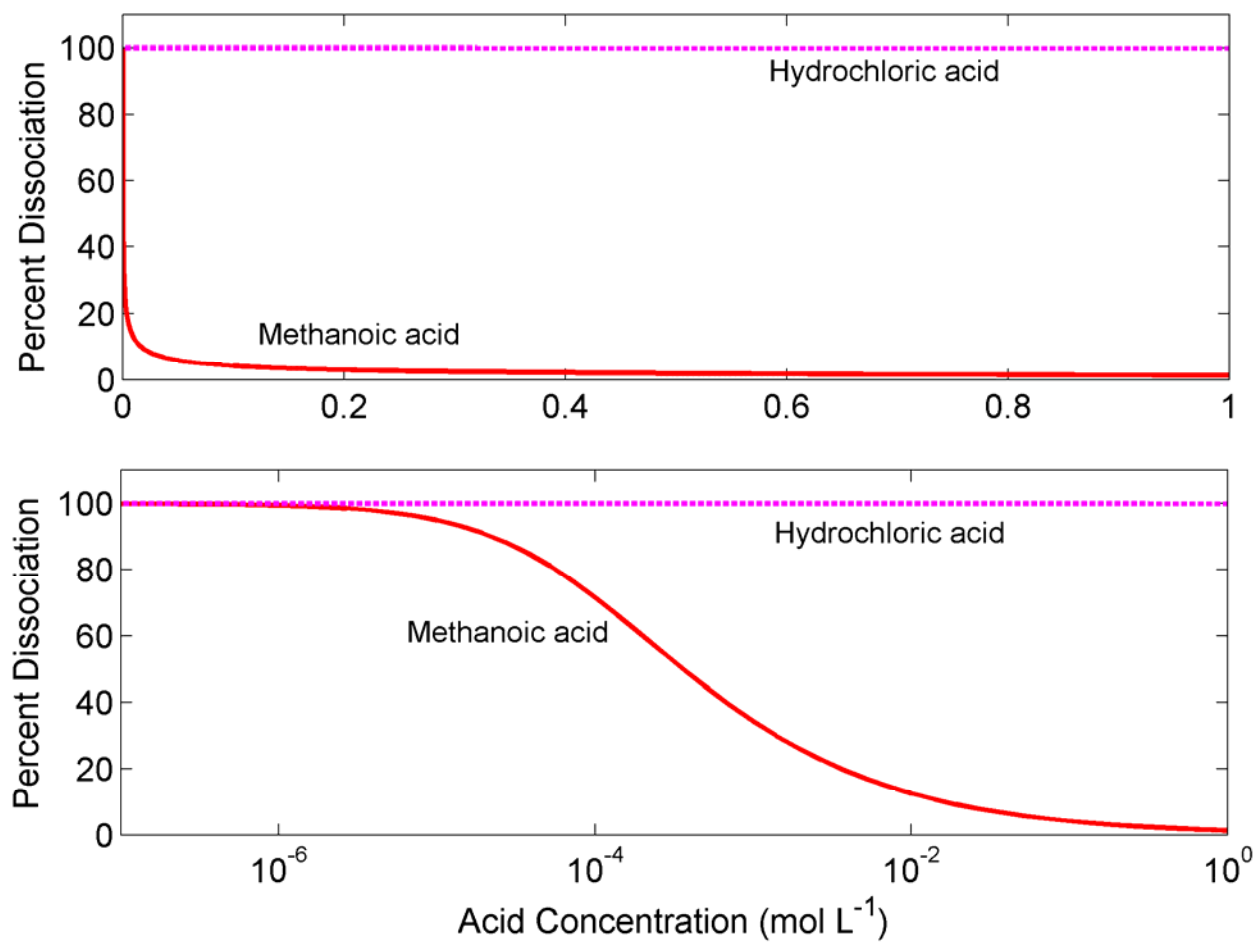
For an initial concentration of methanoic acid of 1.00 mol L^{-1} ,

$$\begin{aligned} x &\cong \sqrt{K_a [\text{HA}]_{\text{initial}}} \\ &= \sqrt{1.8 \times 10^{-4} \times 1.00} = 0.013 . \end{aligned}$$

and the percent dissociation is $100\% \times [\text{HCOO}^-] / [\text{HCOOH}]_{\text{initial}} = 0.013 / 1.00 = 1.3\% .$

A weak acid at *high* concentration is mostly *undissociated*.

A weak acid at *low* concentration is mostly *dissociated*.



At very low concentration (below $10^{-6} \text{ mol L}^{-1}$), *autoionization* of water must be taken into account.

In principle, we must solve *two* equilibrium conditions simultaneously.
However, for such dilute solutions most acids are fully dissociated – all such that $K_a > 100 [\text{HA}]_{\text{initial}}$.

Consider a $10^{-8} \text{ mol L}^{-1}$ solution of hydrochloric acid (or any other monoprotic acid with $K_a > 10^{-6}$).

The acid is fully dissociated resulting in a concentration of hydronium of $10^{-8} \text{ mol L}^{-1}$.

This $10^{-8} \text{ mol L}^{-1}$ hydronium ion concentration provides the initial concentration of hydronium in the autoionization ICE table.

The extent of autoionization reaction is given by solving

$$10^{-14} = (x + 10^{-8})x = x^2 + 10^{-8}x$$

or

$$0 = x^2 + 10^{-8}x - 10^{-14},$$

which has the admissible root, $x = 9.5 \times 10^{-8}$. The equilibrium hydronium concentration is

$$[\text{H}_3\text{O}^+] = x + 10^{-8} = 1.05 \times 10^{-7} \text{ mol L}^{-1}$$

and

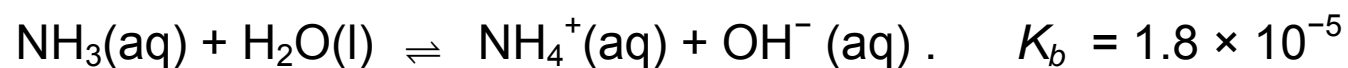
$$\text{pH} = 6.98 .$$

Slightly lower than that of a neutral solution – an acid solution.

Base Association Equilibrium

Weak bases are analogous to weak acids.

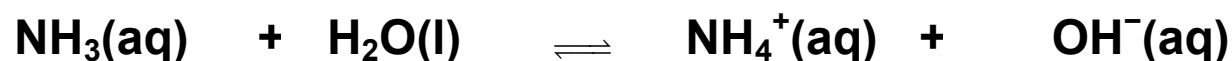
For example,



is the *base association reaction* of ammonia.

Example: What is the pH of a (a) 1.00 mol L^{-1} and (b) $1.00 \times 10^{-3} \text{ mol L}^{-1}$ solution of ammonia, $\text{NH}_3(\text{aq})$?

(a)



Initial	1.00	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$1.00 - x$	x	x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{1.00 - x} = 1.8 \times 10^{-5}$$

The approximation, $1.00 - x \approx 1.00$ is good here.

Therefore,

$$x^2 = 1.8 \times 10^{-5} \times 1.00$$

$$x = \sqrt{1.8 \times 10^{-5}} = 4.2_4 \times 10^{-3}$$

and

$$[\text{OH}^-] = x = 4.2_4 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pOH} = -\log_{10}([\text{OH}^-]) = -\log_{10}(4.2_4 \times 10^{-3}) = 2.37$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.37 = 11.63$$

(b)

	$\text{NH}_3(\text{aq})$	$+ \text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{NH}_4^+(\text{aq})$	$+ \text{OH}^-(\text{aq})$
Initial	1.00×10^{-3}			0	0
Change	$-x$			$+x$	$+x$
Equilibrium	$1.00 \times 10^{-3} - x$			x	x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{1.00 \times 10^{-3} - x} = 1.8 \times 10^{-5}$$

The solution is dilute, $1.00 \times 10^{-3} - x$ cannot be approximated.

$$x^2 + 1.8 \times 10^{-5}x - 1.8 \times 10^{-5} \times 1.00 \times 10^{-3} = 0$$

has solution,

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 + 4 \times 1.8 \times 10^{-5} \times 1.00 \times 10^{-3}}}{2}$$

$$= \begin{cases} 1.2_5 \times 10^{-4} \\ -1.4_3 \times 10^{-4} \end{cases}$$

The admissible solution ($x = 1.2_5 \times 10^{-4}$) gives

$$[\text{OH}^-] = x = 1.2_5 \times 10^{-4} \text{ mol L}^{-1}$$

$$\text{pOH} = -\log_{10}([\text{OH}^-]) = -\log_{10}(1.2_5 \times 10^{-4}) = 3.90$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.90 = 10.10 .$$

Weak bases are mostly unassociated except in dilute solutions – specifically, concentrations comparable to or lower than K_b .

Strength of Acids and Bases

The *strongest* acids have *large* K_a , while weaker acids have smaller K_a . Bases are similarly ordered according to K_b .

$$\text{p}K_a = -\log_{10}(K_a) \quad \text{and} \quad \text{p}K_b = -\log_{10}(K_b)$$

Because of the minus sign, the strongest acids have the *lowest* $\text{p}K_a$ values, while the weakest acids have the *highest* $\text{p}K_a$ values. Similarly, a *lower* $\text{p}K_b$ corresponds to a *stronger* base.

Hydronium, with $\text{p}K_a = 0$, is the dividing line between *strong* acids ($\text{p}K_a < 0$) and *weak* acids ($14 > \text{p}K_a > 0$).

Water is the dividing line between *weak* acids and *very weak* acids ($\text{p}K_a > 14$).

Hydroxide separates *weak* ($14 > \text{p}K_b > 0$) and *strong* ($\text{p}K_b < 0$) bases.

Water separates *weak* and *very weak* bases ($\text{p}K_b > 14$).

	Acid	pK_a	Base	pK_b	
Strong Acids	HI	-10	I^-	24	Very Weak Bases
	$HClO_4$	-10	ClO_4^-	24	
	HBr	-9	Br^-	23	
	HCl	-7	Cl^-	21	
	H_2SO_4	-3	HSO_4^-	17	
	HNO_3	-1.4	NO_3^-	15.4	
	$HClO_3$	-1	ClO_3^-	15	
	H_3O^+	0.00	H_2O	14.00	

Weak Acids	Cl_3CCOOH	0.66	Cl_3CCOO^-	13.34	Weak Bases
	HIO_3	0.78	IO_3^-	13.22	
	H_2SO_3	1.85	HSO_3^-	12.15	
	HSO_4^-	1.99	SO_4^{2-}	12.01	
	H_3PO_4	2.16	H_2PO_4^-	11.84	
	HF	3.20	F^-	10.80	
	HNO_2	3.25	NO_2^-	10.75	
	HCOOH	3.75	HCOO^-	10.25	
	CH_3COOH	4.76	CH_3COO^-	9.24	
	H_2CO_3	6.35	HCO_3^-	7.65	
	H_2S	7.05	HS^-	6.95	
	HSO_3^-	7.2	SO_3^{2-}	6.8	
	H_2PO_4^-	7.21	HPO_4^{2-}	6.79	
	HOCl	7.40	OCl^-	6.60	
	NH_4^+	9.25	NH_3	4.75	
	HCO_3^-	10.33	CO_3^{2-}	3.67	

Very Weak Acids	H₂O	14.00	OH⁻	0.00	Strong Bases
	CH ₃ OH	15.5	CH ₃ O ⁻	-1.5	
	HCCH	25	HCC ⁻	-11	
	H ₂	35	H ⁻	-21	
	NH ₃	38	NH ₂ ⁻	-24	

Relationship between pK_a of an acid and pK_b of its conjugate base:

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{and} \quad K_b = \frac{[OH^-][HA]}{[A^-]}$$

The product of these two expressions is just

$$\begin{aligned}
 K_a K_b &= \frac{[H^+][\cancel{A^-}]}{[\cancel{HA}]} \frac{[\cancel{OH^-}][\cancel{HA}]}{[\cancel{A^-}]} \\
 &= [H^+][OH^-] = K_w = 1.00 \times 10^{-14} .
 \end{aligned}$$

Applying $-\log_{10}$ gives

$$-\log_{10} (K_a K_b) = -\log_{10}(K_w) = 14.00$$

or

$$\text{p}K_a + \text{p}K_b = 14.00$$

Strength of Acids

The relative strength of a neutral acid depends on the relative *stability* of the conjugate base – an *anion*.

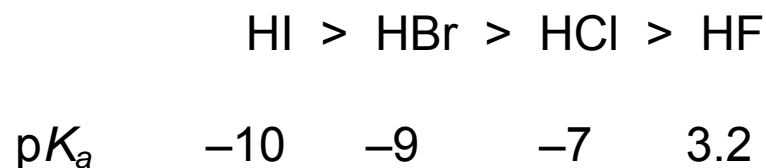
- (1) Anion stability increases with *size* of the atom carrying the charge.
- (2) Anion stability increases with the extent to which *resonance* structures spread out the charge.
- (3) Anion stability increases with *electronegativity* of the atom carrying the negative charge.
- (4) Anion stability increases with the electronegativity of neighboring atoms. The *inductive effect*.

Strength of Binary Acids

HX

The strength of HX acid *increases* as X varies *down* a group.

For example,



According to stability, the conjugate base anions are correspondingly ordered:



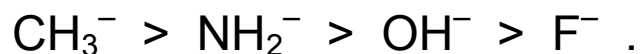
Size effect is the more important going down a group.

Electronegativity of X determines the relative strength of the acids across a period.

The strength of HX acids *increases* as X goes from *left to right* across a period.
For example,



According to stability, the anions are correspondingly ordered:

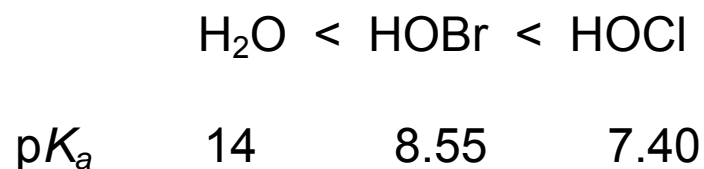


Strength of Oxoacids

Acidic hydrogen is bonded to an oxygen atom.

Resonance structures and the inductive effect are important here.

Consider the following ordering of acids:



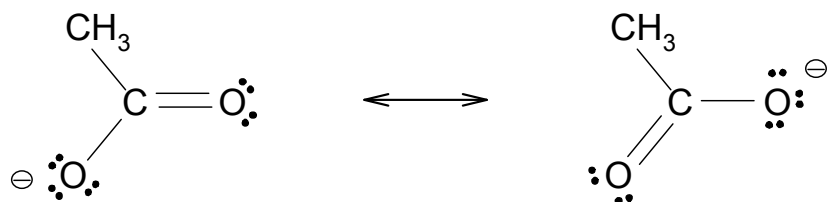
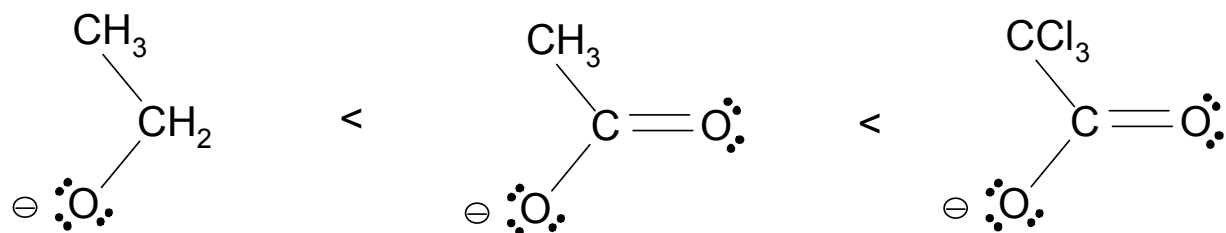
According to anion stability,



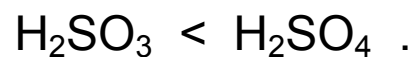
Carboxylic acids are more acidic than alcohols because of the **inductive effect** and **resonance stabilization**.



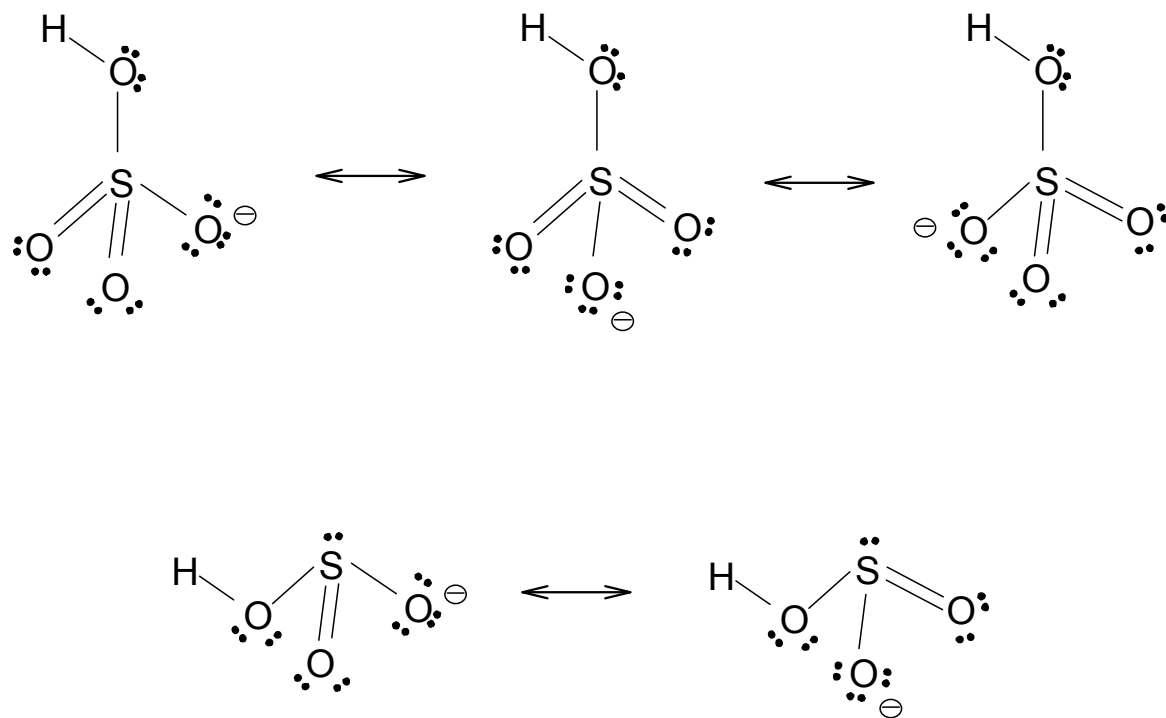
According to anion stability,



The relative strength of sulfurous and sulfuric acid also follows from the **inductive effect** and **resonance stabilization**.



$\text{p}K_a$ 1.85 -3



Polyprotic acids have more than one acidic hydrogen.

$$pK_{a1} < pK_{a2} < \text{etc.}$$

Strength of Bases

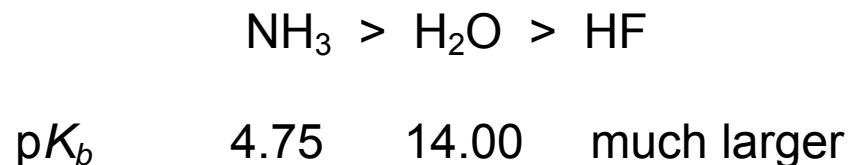
Anionic bases – conjugate bases to neutral acids.

A more stable anion is a weaker base.

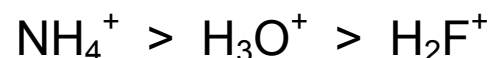
Neutral bases – they become cations when they accept an H^+ .

The strength of the base is determined by the stability of the cation formed.

For example, according to base strength, we have



This is in accord with *stability* of associated *cations* – the *conjugate acid*;



Positive charge is more stable attached to a *less electronegative* element.

Inductive effect:



According to *cation stability*,



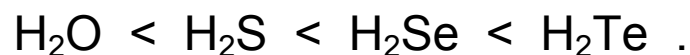
The methyl group *stabilizes* the positive charge – it has more electron density than hydrogen and carbon is *less electronegative* than nitrogen (nitrogen can take electrons density from carbon).

Oxygen *destabilizes* the positive charge because it is *more electronegative* than nitrogen.

Example: Order the following sets of acids and bases according to increasing strength as an acid or base, respectively:

- (a) H_2O , H_2S , H_2Se , H_2Te (as acids)
- (b) SiH_4 , PH_3 , H_2S , HCl (as acids)
- (c) CH_3COOH , Cl_3CCOOH , BrCH_2COOH , ClCH_2COOH (as acids)
- (d) $\text{CH}_3\text{CH}_2\text{NH}_2$, NH_3 , NHCl_2 (as bases)

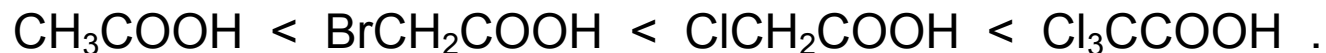
(a) According to increasing acid strength,



(b) According to increasing acid strength,



(c) According to increasing acid strength,



(d) According to increasing strength as bases,

