The chemical reaction will run forward if

$$\Delta G = \sum_{i=k+1}^{m} \nu_i \mu_i - \sum_{i=1}^{k} \nu_i \mu_i < 0 \qquad (8.14)$$

and backward if $\Delta G > 0$. So ΔG is the net chemical force driving the reaction. More accurately, ΔG is the change in the potential energy, the Gibbs free energy. At equilibrium,

$$\Delta G = 0.$$

The standard free-energy change is

$$\Delta G^\circ = \sum_{k+1}^{m} \nu_i \mu_i^0 - \sum_{i=1}^{k} \nu_i \mu_i^0 . \qquad (8.16)$$

Recall that

$$\mu_i = kT \ln(c_i/c_0) + \mu_i^0(T) \qquad (8.3)$$

at least for dilute solutions, so that

$$\Delta G = \Delta G^\circ + kT \ln\left[\prod_{k+1}^{m} (c_i/c_0)^{\nu_i} \prod_{1}^{K} (c_i/c_0)^{-\nu_i} \right],$$

The equilibrium constant is

$$K_{eq} = e^{-\Delta G^0 / kT}$$

for a general reaction. If we set $c_0 = 1M$, then at equilibrium

$$0 = \frac{\Delta G}{kT} = \frac{\Delta G^0}{kT} + \frac{kT}{kT} \ln\left(\frac{\prod_{k+1}^{m} [X_i]^{\nu_i}}{\prod_{1}^{k} [X_i]^{\nu_i}} \right)$$

so that

$$-\frac{\Delta G^0}{kT} = \ln\left(\frac{\prod_{k+1}^{m} [X_i]^{\nu_i}}{\prod_{1}^{k} [X_i]^{\nu_i}} \right).$$

Taking the exponential of both sides, we get

$$K_{eq} = \frac{[X_{k+1}]^{\nu_{k+1}} \cdots [X_m]^{\nu_m}}{[X_1]^{\nu_1} \cdots [X_k]^{\nu_k}} \qquad (8.17)$$

which is the <u>mass-action</u> rule.

Here $[X_i] = c_i / 1M$.

$\boxed{8E}$ $\Delta G^0_{f\alpha} = \mu^0_\alpha - \mu_\alpha^{00}$ so

$$\mu^0_2 - \mu^0_1 = \mu^0_2 - \mu^{00}_2 - (\mu^0_1 - \mu^{00}_1)$$

because $\mu_2^{00} = \mu_1^{00}$ — since both the reactants and the products are made from the same set of elemental constituents.

$\boxed{8F}$ $$e^{-\frac{\Delta G^0}{kT}} = \left(10^{\log_{10} e}\right)^{-\frac{\Delta G^0}{kT}}$$

$$= 10^{-\frac{\Delta G^0}{kT}\log_{10} e} = 10^{-x\frac{\Delta G^0}{kT}}$$

where $10^x = e = (e^{\ln 10})^x = e^{x \ln 10}$.

So $x = 1/\ln 10$. So

$$e^{-\frac{\Delta G^0}{kT}} = e^{-\frac{\Delta G^0}{\ln 10\, kT}}.$$ Now $kT = 4{,}1 \times 10^{-21}$ J

and $4{,}2\text{J} = 1$ cal, so with $\ln 10 = 2{,}303$

$$\ln 10\, kT = 2{,}303 \cdot 4{,}1 \cdot 10^{-21}\text{J}\ \frac{1\,\text{cal}}{4{,}2\,\text{J}} \times \frac{6\,10^{23}}{\text{mole}} = 1{,}35\ \text{kcal/mole}$$

So

$$K_{eq} = e^{-\frac{\Delta G^\circ}{kT}} = 10^{-\frac{\Delta G^\circ}{1.35\,kcal/mole}}.$$

Chemists have special rules for water and $[H^+]$. In dilute solutions, $[H_2O] \cong 55$, so the ratio

$$\frac{[H_2O]}{c_0} = 1$$

if we take $c_0 = 55\,M$ for water. Then

$\frac{c_{H_2O}}{c_{0\,H_2O}} = 1$ drops out of the mass-action formula (8.17).

Also, chemists set $c_{0\,H^+} = 10^{-7}\,M$, so for dilute solutions

$c_{H^+}/c^0_{H^+} \approx 1$ drops out of (8.17).

But we always use $[X] = c_X / 1M$.

When one uses special conventions, one writes $\Delta G'^0$ and K'_{eq}. Sometimes, standard conditions are $T = 25°C$ and $P = 10^5 Pa$.

A proton in water binds tightly to the O of one H_2O molecule, forming the <u>hydronium ion</u> H_3O^+. So $[H^+]$ really means the concentration $[H_3O^+]$. Similarly, Na^+ in water is part of a <u>hydrated ion</u>, and $\mu^0_{Na^+}$ includes the free-energy cost to assemble the whole thing.

When reactions run on timescales short compared to those of an experiment, the solution reaches equilibrium at $\Delta G = 0$.

Le Châtelier's principle: if one adds X_i to an equilibrium mixture, the reaction will run in a direction that partially reduces $[X_i]$.

Keep in mind that in equilibrium reactions are going both ways — but so as to keep the c_i's constant.

Complex equilibria and reaction rates:

Consider the reaction

$$X_2 + Y_2 \underset{k_-}{\overset{k_+}{\rightleftharpoons}} 2XY \qquad (8.20)$$

where

$$\left.\begin{aligned} r_+ &= k_+ C_{X_2} C_{Y_2} \\ \text{and} \quad r_- &= k_-(C_{XY})^2 \end{aligned}\right\} (8.19)$$

so that $r_+ = r_-$ gives $(C_{XY})^2/(C_{X_2}C_{Y_2}) = K_{eq}$ (8.21)

The equilibrium condition (8.21) is correct, but the kinetics — the rate at which mixtures of X_2 and Y_2 in a dilute solution produce $2XY$ depends on the details of the reactions. If the process is simply

$$X_2 + Y_2 \rightleftarrows 2XY$$

then doubling $[X_2]$ will double the rate, as will doubling $[Y_2]$. But if the process is more like

1) $X_2 + X_2 \rightleftarrows 2X + X_2$ slow

2) $X + Y_2 \rightleftarrows XY_2$ fast

3) $XY_2 + X \rightleftarrows 2XY$ fast

then doubling $[X_2]$ quadruples the rate.

The slow step is the bottleneck or the rate-limiting step. It controls the overall rate, but not the ratio of c_i's at equilibrium. In fact, each of the three processes must be in equilibrium:

$$\frac{c_X^2\, c_{X_2}}{(c_{X_2})^2} = K_{eq,1}\, c_0 \,, \qquad \frac{c_{XY_2}}{c_X\, c_{Y_2}} = \frac{K_{eq,2}}{c_0} \,,$$

& $$\frac{(c_{XY})^2}{c_{XY_2}\, c_X} = K_{eq,3}$$ so that

$$K_{eq} = K_{eq1}\, c_0 \cdot \frac{K_{eq2}}{c_0} \cdot K_{eq3} = K_{eq1}\, K_{eq2}\, K_{eq3}$$

$$= \frac{c_X^2\, c_{X_2}}{(c_{X_2})^2}\, \frac{c_{XY_2}}{c_X\, c_{Y_2}}\, \frac{(c_{XY})^2}{c_{XY_2}\, c_X} = \frac{(c_{XY})^2}{c_{X_2}\, c_{Y_2}}$$

which is (8.21) again.

Equilibrium does not depend on the details of the intermediate steps. (Idea 8.23)

The early Earth was not in equilibrium.

If one mixes atoms in proportions $C:H:N:O = 2:10:1:8$ at 500 °C, eventually one gets H_2O, CO_2, N_2, CH_4 big-time but H_2 at 1%, acetic acid, CH_3COOH, at 10^{-10} and lactic acid, $CH_3CHOHCOOH$, at 10^{-24}. The exponential in $K_{eq} = \exp(-\Delta G^0/kT)$ dramatically suppresses compounds with bigger ϵ's.

Dissociation. When Na meets Cl, the outer, 3s, electron of Na jumps to the Cl making Na^+ and Cl^- which are bound by

$$qV = \frac{e^2}{4\pi\epsilon_0 d} \simeq 10^2 kT$$

at $d \simeq 0.3$ nm, which is the spacing in rock salt, NaCl. So we'd need $T \sim 10^2 \cdot 300\,K = 30{,}000\,K$ to vaporize rock salt into a plasma of Na^+ and Cl^-.

But NaCl in water readily dissolves because ϵ_0 is replaced by $\epsilon \simeq 80\,\epsilon_0$, reducing qV to something like kT_r. And S rises as the hydrated ions Na^+ and Cl^- wander throughout the water.

Most polar molecules are soluble in water. Thus alcohols with $-OH$ groups and amines with $-NH_2$ amine groups usually dissolve in water. But hydrocarbons and oils usually don't.

The reaction

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (8.24)$$

at equilibrium has $c_{H^+} = c_{OH^-} = 10^{-7}$ M. Since c_{H_2O} stays at ~55 M, chemists use

$$K_w \equiv [H^+][OH^-] = (10^{-7})^2 = 10^{-14} \text{ M}. \quad (8.25)$$

This is the <u>ion product of water</u> at room temperature. If we add HCl to pure water, [H+] shoots up to 10^{-1} or 10^{-2} M and so (8.25) forces [OH-] down to 10^{-13} or 10^{-12} M.

If we add lye, NaOH, to water, the NaOH dissociates into Na^+ and OH^-. Thus $[OH^-]$ rises, and so

$$[H^+] = \frac{10^{-14}}{[OH^-]}$$

must drop. The pH is

$$pH = -\log_{10}[H^+]. \qquad (8.26)$$

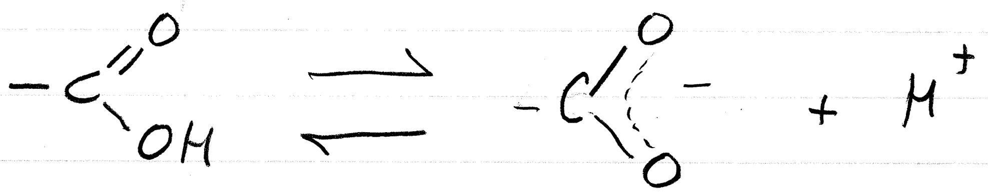
Pure water has

$$pH = -\log_{10}[H^+] = -\log_{10} 10^{-7} = 7,$$

Adding an acid raises $[H^+]$ and so lowers the pH below 7. Adding a base raises $[OH^-]$, lowers $[H^+]$, and raises the pH above 7.

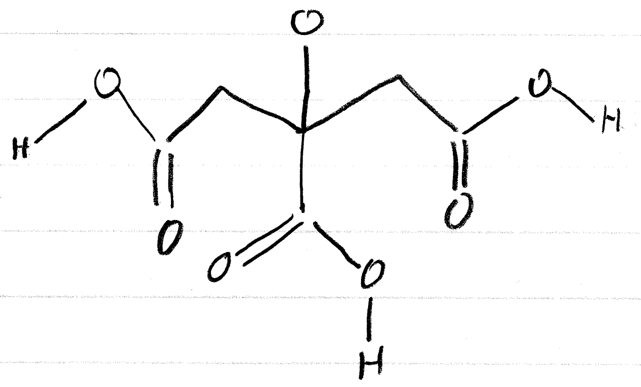
Solutions with $pH < 7$ are <u>acidic</u>; those with $pH > 7$ are <u>basic</u>.

An organic acid has a carboxyl group



which partially dissociates into $-COO^-$ and H^+.

Acetic acid, CH_3COOH (aka vinegar), lemon juice, aka citric acid $C_6H_8O_7$, RNA, and DNA are examples. Citric acid has three carboxyl groups:



DNA dissociates into many protons and a macroion with two negative charges per basepair. All these organic acids are weaker than HCl; they don't lose all their protons. The pK of acetic acid is 4.76, while that of the much stronger phosphoric acid H_3PO_4 is 2.15. Recall (8.12) & (8.17) that for $HR \rightleftharpoons H^+ + R^-$

$$pK = -\log_{10} K_{eq} = -\log_{10} \frac{[H^+][R^-]}{[HR]}$$

so the smaller the pK, the stronger the acid. Acetic acid is a <u>weak</u> <u>acid</u>.

Any molecule that absorbs protons is a base and raises the pH. Thus the amine group $-NH_2$ takes up protons

$$-NH_2 + H^+ \rightleftharpoons -NH_3^+ \qquad (8.27)$$

Ammonia NH_3 in water grabs a proton

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

and at pH 7 about 99% of the ammonia molecules are protonated.

Bases can be weak or strong. NaOH (lye) is a strong base.

If we add equal amounts of HCl and NaOH, then the pH will not change, but the solution will become salty.

But if we added NaOH and acetic acid, we'd need much more acid to keep the pH from changing.

A solution of a weak acid and "its conjugate base" resists changes in pH.

For example, acetic acid is a weak acid, so a solution of acetic acid and sodium acetate $NaCH_3COO$ has a pH that changes only slightly if an acid or a base is added. It is called a buffer solution. To see how this works, let's use HA for acetic acid and NaA for sodium acetate. Then HA's equilibrium constant

$$\frac{[H^+][A^-]}{[HA]} = K_{HA}$$

is much smaller than that of NaA

$$\frac{[Na^+][A^-]}{[NaA]} = K_{NaA} \, ,$$

$$K_{HA} << K_{NaA} \, .$$