Biochemist's Standard State

(typically let $a_{water} \approx 1$) ← we saw good reason for this last time

Problem: water can dissociate to yield H^+ (ie water comes at different pH's)

Solution: Choose pH=7 as the standard state (reference), so that $a_{H^+} = 1$

Denote parameters using this reference as $\Delta G'$ and $\Delta G^{o\prime}$

You can calculate at other pH's, it's just that the reference state is pH=7

$$HOAc\ (aq) \rightleftharpoons H^+\ (aq) + OAc^-\ (aq)$$

"real" $K = \dfrac{(a_{H^+})(a_{OAc^-})}{a_{HOAc}} = \dfrac{(\gamma_+ C_{H^+})(\gamma_- C_{OAc^-})}{\gamma_{HOAc}\, C_{HOAc}}$

$$= \frac{\gamma_+\gamma_-}{\gamma_{HOAc}} \frac{C_{H^+} C_{OAc^-}}{C_{HOAc}} = \frac{\gamma_+\gamma_-}{\gamma_{HOAc}} K_c$$

and

$$K_c = \frac{(C_{H^+})(C_{OAc^-})}{C_{HOAc}}$$

$HOAc(aq) \rightleftharpoons H^+(aq) + OAc^-(aq)$

So $K = \left(\frac{\gamma_+ \gamma_-}{\gamma_{HOAc}}\right) K_c$

↖ depends on concentration — approaches 1 at very dilute

ie. at very dilute, $K \rightarrow K_c$ (approaching ideality)

γ_+ and γ_- ← Cannot measure independently
(H^+) (OAc^-)

Take an "average" $\gamma_\pm = (\gamma_+ \gamma_-)^{1/2}$

N.B. As discussed before, solvated (aqueous) ions interact strongly with the solvent and therefore are very non-ideal.

In 0.1 M NaCl, $\gamma_\pm = 0.78$
in 0.01 M NaCl, $\gamma_\pm = 0.90$

So ΔG° really refers to:

$HOAc(1M^*, aq) \longrightarrow H^+(1M^*, aq) + OAc^-(1M^*, aq)$

* but with properties at infinite dilutions (0 concentration)

So to do this at a real 1M each, you'll get different results...

(we'll see later how to resolve this)

Test:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

For all 1M,

$$\Delta G = \Delta G^\circ + RT \ln \frac{(1M)(1M)}{(1M)}$$
$$= \Delta G^\circ + RT \ln (1)$$
$$= \Delta G^\circ + 0$$
$$= \Delta G^\circ$$

Back to definition

If we dilute <u>everything</u> by 10,000-fold (10^{-4} M)
then

$$\Delta G = \Delta G^\circ + RT \ln \frac{(10^{-4})(10^{-4})}{10^{-4}}$$

$$= \Delta G^\circ + RT(-4) \ln 10$$

$$\Delta G = \Delta G^\circ - 22.82 \text{ kJ}$$

ΔG° is <u>lower</u>. (more negative), so
the reaction goes to the <u>right</u>.

Does LeChatelier agree?

$$\text{Lower} \rightleftharpoons (\text{Lower})(\text{Lower})$$

depleting more
(total) on the right
Le Chatelier says then that rxn → right.

Good!

Let's look at a hydrolysis reaction:

$$H_2O(l) + CH_3COOCH_2CH_3(q) \rightleftharpoons CH_3COOH(aq) + CH_3CH_2OH(aq)$$

$$H_2O(l) + EtOAc \rightleftharpoons HOAc + EtOH$$

$$K = \frac{a_{HOAc}\, a_{EtOH}}{a_{H_2O}\, a_{EtOAc}} = \frac{\gamma_{HOAc}\, \gamma_{EtOH}}{\gamma_{H_2O}\, \gamma_{EtOAc}} \frac{C_{HOAc}\, C_{EtOH}}{C_{H_2O}\, C_{EtOAc}}$$

in very dilute solutions, $a_{H_2O} \to 1$ and $\gamma_i^\circ \to 1$

$$\therefore K \to \frac{C_{HOAc}\, C_{EtOH}}{C_{EtOAc}}$$ (and ignore the water)

But γ_i° and K (because of a_{H_2O}) depend on the choice of the standard state.

e.g. if we chose to express a_{H_2O} as 55 M instead of 1

then K would change
γ_i would change

<u>but</u> $\Delta G \to$ would not change
ie. <u>reality</u> does not depend on our choice of reference state.

K would be different, but we'd specify that $C_{H_2O} = 55M$, so things would balance.

SHIFT GEARS

Ideal Solutions (oh, thank you!)

All right, let's assume/pretend that everything is dilute enough that we can ignore non-ideality.

Let's get to business →

How to use K_{eq} (or ΔG°)

Problem: Add C_A moles HOAc (acetic acid)
plus C_S moles of NaOAc (sodium acetate)
to water,
to a final volume of 1 L.

Lots of things will happen, and we'll have a mix of:

$HOAc,\ H^+,\ OAc^-,\ Na^+,\ OH^-$ (plus H_2O)

5 unknowns requires 5 independent equations

Mass Balance

(1) $[Na^+] = C_S$ (assume NaCl completely dissociates - yes)

(2) $[HOAc] + [OAc^-] = C_A + C_S$

Charge Balance

(3) $[Na^+] + [H^+] = [OAc^-] + [OH^-]$

Equilibrium

$$K_{HOAc} = \frac{[H^+][OAc^-]}{[HOAc]} \qquad (4)$$

$$K_{H_2O} = \frac{[H^+][OH^-]}{1 \leftarrow [H_2O]} \qquad (5)$$

Special Case:

What are all of these in 0.100 M HOAc? (ie. no added NaOAc, $C_S = 0$)

(1) $[Na^+] = C_S = 0$

(2) $[HOAc] + [OAc^-] = C_A = 0.100\ M$

(3) $0 + [H^+] = [OAc^-] + [OH^-]$

(4) $K_{HOAc} = \frac{[H^+][OAc^-]}{[HOAc]} = 1.8 \times 10^{-5}$

(5) $K_{H_2O} = [H^+][OH^-] = 1.00 \times 10^{-14}$

Make assumptions (could solve explicitly, but approximations simplify our life)

Assume pH < 7.0, the $[H^+] >> [OH^-]$

↳ then (3) becomes $[H^+] = [OAc^-]$

Classic approach with some algebra:

Let $[H^+] = x$, the unknown: ∴ $[H^+] = x$ $[Na^+] = 0$ (1)

$[OAc^-] = x$ (3)

$[HOAc] = 0.1\ M - x$ (2)

∴ Equation 4 tells us

$$K_{HOAc} = 1.8 \times 10^{-5} = \frac{(x)(x)}{0.1 - x}$$

$$x^2 = (1.8 \times 10^{-5})(0.1 - x)$$

$$x^2 + (1.8 \times 10^{-5})x - (0.1)(1.8 \times 10^{-5}) = 0$$

(Remember units are not there, or Molar depending on our being "correct" or practical, respectively.)

Solve quadratic, $x = 1.33 \times 10^{-3}$

See example 4.4 (pp 144-145)

$$[H^+] = [OAc^-] = 1.33 \times 10^{-3}$$

$$[HOAc] = 0.1 - (1.33 \times 10^{-3}) = 9.87 \times 10^{-2}$$

$$[OH^-] = \frac{K_{H_2O}}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.33 \times 10^{-3}} = 7.52 \times 10^{-12}$$

Check assumptions

$[H^+] >> [OH^-]$? Yes $(1.33 \times 10^{-3}) >> (7.52 \times 10^{-12})$

↑ (equals $[OAc^-]$)

GOOD — NOT GROSSLY WRONG!

Same situation, but in 0.200M NaOAc:

Example 4.5 pp 146-147

$x = 1.05 \times 10^{-5}$

$[OH^-] = [HOAc] = 1.05 \times 10^{-5}$

$[Na^+] = [OAc^-] = 0.200$

$[H^+] = 9.52 \times 10^{-10}$

This is all ALGEBRA

Sometimes ugly algebra, but
algebra none the less!

Approximations can simplify
Or computers can solve numerically.

Be careful that "n" equations are truly independent

e.g. we might add another equation to the above,

$$K_B = \frac{[HOAc][OH^-]}{[OAc^-]}$$

but

$$\rightsquigarrow K_A K_B = \frac{[H^+][OAc^-]}{[HOAc]} \times \frac{[HOAc][OH^-]}{[OAc^-]} = [H^+][OH^-] = K_{H_2O}$$

Three equations, but only two are independent