Put up before class:

C_A moles HOAc (acetic acid)
C_S moles NaOAc (sodium acetate) – dissociates completely to water, final volume = 1 L

Mass balance:

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

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

Charge Balance:

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

Equilibria:

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

(5) $K_{H_2O} = [H^+][OH^-] = 1.0 \times 10^{-14}$

Solve – classic approach → assume $pH < 7.0$
Then $[H^+] >> [OH^-]$

(3)

SKIP

Simple example: 0.100 M HOAc (No NaOAc)

NOT USEFUL

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

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

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

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

(5) $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

Trick to make easier → this is an acid dissociating,
so $[H^+] >> [OH^-]$

∴ (3) $[H^+] \approx [OAc^-]$ (cannot ignore $[OH^-]$ in (5))

let $x = [H^+]$ leads also to $[OAc^-] = x$

(2) $[HOAc] = 0.100\,M - x$

(4) $K_{HOAc} = \frac{x \cdot x}{0.10 - x} = 1.8 \times 10^{-5}$

$x^2 = (0.10)K_{HOAc} - K_{HOAc}\,x$

$x^2 + K_{HOAc}\,x - (0.10)(K_{HOAc}) = 0$

$x = \frac{-K_{HOAc} \pm \sqrt{(K_{HOAc})^2 + 4(0.10)K_{HOAc}}}{2}$

$x = 1.33 \times 10^{-3}\,M = [H^+]$ (→ $10^{-7}\,M$)

Simple Example #2 — 0.200 M NaOAc

(1) $[Na^+] = 0.200M$

(2) $[HOAc] + [OAc^-] = 0.200M$

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

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

(5) $K_w = [OH^-][H^+] = 1.0 \times 10^{-14}$

Approx/assume $[Na^+] >> [H^+]$

(3) $0.200 = [Na^+] = [OH^-] + [OAc^-]$

(2) $0.200 = [HOAc] + [OAc^-]$

$\therefore [OH^-] = [HOAc]$

Let $x = [HOAc] = [OH^-]$

(2) $[OAc^-] = 0.200M - x$

(5) $[H^+] = 10^{-14}/x$

$\Rightarrow$ (4) $1.8 \times 10^{-5} M = \frac{(\frac{10^{-14}}{x})(0.200M - x)}{x}$

(K_a) $\Downarrow (K_w)$

$\frac{x(1.8 \times 10^{-5} \times 10^{14})}{x} = \frac{0.200M - x}{x}$

~~$(K_a)(K_w)x^2 - (0.200 \times 10^{-14})(\frac{1}{x}) - 10^{-14} = 0$~~

$(K_a)(K_w)x^2 + x - 0.200M = 0$

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

$[H^+] = \frac{10^{-14}}{1.05 \times 10^{-5}} \approx 10^{-9}$

Temperature Dependence of $\Delta G / K$

If ΔH independent of Temperature, then

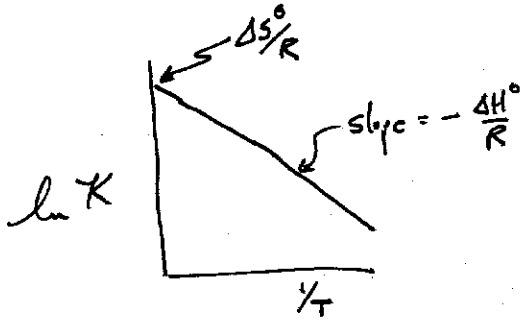
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Ratio →

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Common to plot $\ln K$ vs. $\frac{1}{T}$



Better to fit exactly

$$K = e^{-\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}}$$

More real/complicated → if ΔH° depends on T
then must include this dependence

Rest of Chapter is lots of applications

Except: Galvanic Cells — Electrochemistry

$H = E + PV$ $\quad G = H - TS$

$$G = E + PV - TS$$

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad (\text{Const } T \text{ and } P)$$

$$\Delta G = q_{REV} + w_{REV} + P\Delta V - T\Delta S$$

But $q_{REV} = T\Delta S$ $\quad \left(\Delta S = \frac{q_{REV}}{T}\right)$

So

$$\Delta G = w_{REV} + P\Delta V$$

$w_{P\Delta V} = -P\Delta V$

$$= w_{REV} - w_{P\Delta V}$$

= maximum useful work

Electrical Work

$$-\Delta G = -w_{\text{reversible, electrical}}$$

$-\Delta G$: decrease in system free energy

$w_{\text{reversible, electrical}}$: work done by the system

$$w_{\text{electrical}} = -EIt \quad \text{(Chapter 2)}$$

E: Voltage, I: Current, t: time

but $I \cdot t$ = charge moved
(# moles of electrons)

$\therefore W_{electrical} = -\mathcal{E} n$

[Moving electrons against a voltage ~~gradient~~ (force)]

$$\Delta G = -n\mathcal{E}$$

Units = electron-volts

n = # moles of electrons

$\mathcal{E}$ = voltage of the cell

One mole of electrons moving 1 cm in a field of 1 V cm^{-1} aquires/requires 96.485 kJ/mole

$$\therefore \Delta G = \underbrace{-96.485 n\mathcal{E}}_{kJ/mol} = \underbrace{-n\mathcal{E}F}_{joules/mole}$$

Book shows us (read it!) that the temperature dependence of $\mathcal{E}$ tells us about ΔH and ΔS

$\mathcal{E}$ is directly proportional to $\Delta G/n$

tells us about free energy.
Those in the bioinorganic field use $\mathcal{E}$ to talk about potential energy.

Photosynthesis, Respiration, Microbial respiration/metabolism

Can use E° in a similar way to the way we use G° to predict ΔG.

(or $E^{\circ\prime}$ and $G^{\circ\prime}$) Table 4.4

Similarly

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

Nernst Equation

You learned to use this in General Chemistry

Cytochrome c Oxidase

$\gamma_\pm$ → activity coefficients for ions

Remember that for $HCl \rightarrow H^+ + Cl^-$

$$\gamma_\pm = (\gamma_+ \gamma_-)^{1/2}$$

$\gamma_\pm < 1$ because the effective concentration of H^+ is reduced by Cl^- and vice versa.

For $H_2SO_4 \rightarrow H^+ + HSO_4^- \rightarrow 2H^+ + SO_4^{2-}$

$$\gamma_\pm = (\gamma_+^2 \gamma_-)^{1/3}$$

etc.