10/3/01

Acetic Acid — Classic Example

$$CH_3COOCH_2CH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3CH_2OH$$

$$EtOAc + H_2O \rightleftharpoons HOAc + EtOH$$

<u>Rigorously:</u>

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

$$= \frac{C_{HOAc}\, C_{EtOH}}{C_{EtOAc}\, X_{H_2O}} \cdot \frac{\gamma_{HOAc} \cdot \gamma_{EtOH}}{\gamma_{EtOAc} \cdot \gamma_{H_2O}}$$

($X_{H_2O} \to 1.0$; $\frac{\gamma_{HOAc} \cdot \gamma_{EtOH}}{\gamma_{EtOAc} \cdot \gamma_{H_2O}} \approx 1.0$ in dilute solutions)

$$K \approx \frac{C_{HOAc}\, C_{EtOH}}{C_{EtOAc}}$$

<u>KEY CONCEPT</u> a_{HOAc} depends on a_{EtOAc}, a_{EtOH}, etc but <u>if</u> everyone is <u>dilute</u> enough, the dependence is small.

PRACTICAL Add C_A moles acetic acid $(HOAc)_{init}$ and C_S moles sodium acetate $(NaOAc)_{init}$ to water, w/ final volume =

Rules to use

Mass balance: ~~$[Na^+] = C_S$~~ $[HOAc] + [OAc^-] = C_A + C_S$

Charge balance: $[Na^+] + [H^+] = [OAc^-] + [OH^-]$

Equilibria: $K_{HOAc} = \frac{[H^+][OAc^-]}{[HOAc]} = 1.8 \times 10^{-5}$

Reveals a "coupled" reaction $H_2O \rightleftharpoons H^+ + OH^-$ ← $K_{H_2O} = [H^+][OH^-] = 1.0 \times 10^{-14}$

Q: Why not $K_{H_2O} = \frac{[H^+][OH^-]}{[H_2O]}$?

More worked-through examples pp. 145-150

Solve and eliminate

5 Unknowns: $[Na^+]$, $[HOAc]$, $[OAc^-]$, $[H^+]$, $[OH^-]$,
4 Equations — NOT GOOD

But we know the NaOAc dissociates completely. Some OAc^- may combine w/ H^+, but all Na^+ will stay dissociated.

5^{th} Equation: $[Na^+] = C_S$ Mass Balance

Algebra (<u>only</u>): $[Na^+] = C_S$

Start w/ simple: $[OH^-] = \dfrac{K_{H_2O}}{[H^+]}$

$[OAc^-] = C_A + C_S - [HOAc]$

<u>Substitute into remaining</u>

(1) $C_S + [H^+] = C_A + C_S - [HOAc] + \dfrac{K_{H_2O}}{[H^+]}$ ← 10^{-14} M; ← 10^{-7} M?; → 0

(2) $K_{HOAc}[HOAc] = [H^+](C_A + C_S - [HOAc])$

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(1) $[HOAc^-] = C_A - [H^+]$

into (2) → $K_{HOAc}(C_A - [H^+]) = [H^+](C_A + C_S - (C_A - [H^+]))$

$K_{HOAc}(C_A - [H^+]) = [H^+](C_S + [H^+])$

$K_{HOAc}C_A - K_{HOAc}[H^+] - C_S[H^+] - [H^+]^2 = 0$

$[H^+]^2 + (K_{HOAc} + C_S)[H^+] - K_{HOAc}C_A = 0$

<u>Approx</u>

$(K_{HOAc} + C_S)[H^+] = K_{HOAc}C_A$

$[H^+] = \dfrac{K_{HOAc}C_A}{K_{HOAc} + C_S}$

Exact

$[H^+] = \dfrac{-(K_{HOAc} + C_S) + \sqrt{(K_{HOAc} + C_S)^2 + 4K_{Ho}}}{2}$

$[H^+] = \frac{1}{2}\left[-(K_{HOAc} + C_S) + \sqrt{(K_{HOAc} + C_S)^2 + 4K_{HOAc}}\right.$

↑ Why (+)?

Temperature Dependence of the Equilibrium Constant

$$\frac{d\Delta G}{dT} = -\Delta S \qquad (P = \text{constant},\ C_p \approx 0)$$

At standard state

$$\frac{d\Delta G^\circ}{dT} = -\Delta S^\circ$$

$$\frac{d(-RT\ln K)}{dT} = -\Delta S^\circ$$

$$-RT\frac{d\ln K}{dT} - \left(R\ln K\frac{dT}{dT}\right) = -\Delta S^\circ$$

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

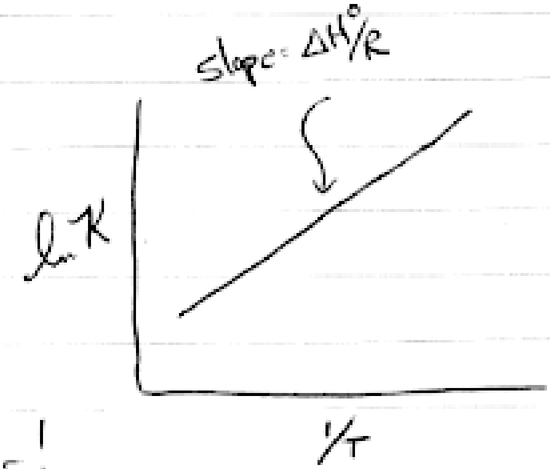
$$-RT^2\frac{d\ln K}{dT} = -T\Delta S^\circ + RT\ln K$$

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

$$= -T\Delta S^\circ - (\Delta H^\circ - T\Delta S^\circ)$$

$$= -\Delta H^\circ$$

$$\frac{d\ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\circ}{R}$$



If $\Delta H^\circ < 0$ (exothermic)
then $K\uparrow$ as $T\downarrow$

$A + B \rightleftharpoons C + D + \text{heat}$

↖ Le Chatelier!

If ΔH° is constant w/ T

$$\int d \ln K = -\frac{\Delta H^\circ}{R} \, d\left(\frac{1}{T}\right)$$

[illegible] =

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

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

Another form of van't Hoff