The Kinetic Salt Effect

not just for diffusion-limited reactions

$$A^{z_A} + B^{z_B} \rightleftharpoons \{AB\}^{z_A+z_B} \longrightarrow \text{products}$$

strictly true only for activated reactions

$$\text{rate} = k[A][B] = k_R[\{AB\}]$$

For concentrated solutions

$$K_{\{AB\}} = \frac{[\{AB\}]}{[A][B]} \cdot \frac{\gamma_{AB}}{\gamma_A \gamma_B}$$

$$\Rightarrow \quad k = k_R \frac{[\{AB\}]}{[A][B]} = k_R K_{\{AB\}} \frac{\gamma_A \gamma_B}{\gamma_{AB}} = k_0 \frac{\gamma_A \gamma_B}{\gamma_{AB}}$$
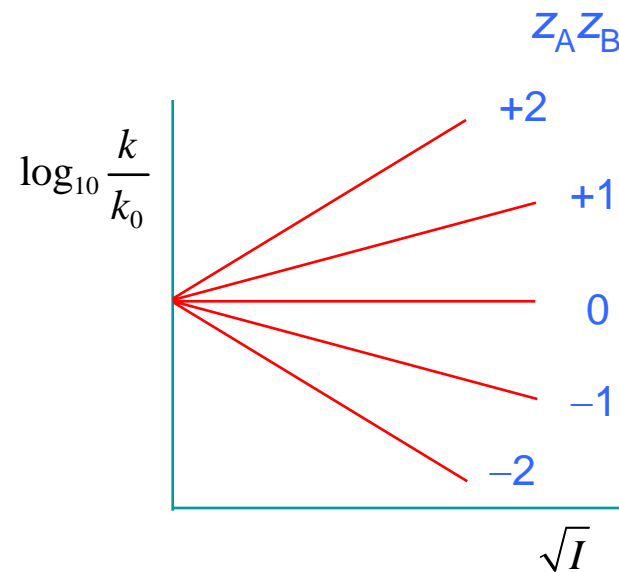
According to Debye-Hûckel $\quad \log_{10} \gamma_i = -0.509 z_i^2 \sqrt{I}$

Ionic strength $\quad I = \tfrac{1}{2} \sum_i [X_i] z_i^2$

$$\log_{10} k = \log_{10} k_0 - 0.509 \left[z_A^2 + z_B^2 - (z_A + z_B)^2 \right] \sqrt{I}$$

$$\log_{10} \frac{k}{k_0} = 1.02 z_A z_B \sqrt{I}$$

Used to distinguish transients, such as H, e^-_{aq}, Mu

The Kinetic Salt Effect – 2

There are small effects even for uncharged reactants.

Suppose A is charged $\qquad \log_{10} \gamma_A = -Cz_A^2 \sqrt{I} + b_A I$

and B is not $\qquad\qquad \log_{10} \gamma_B = -b_B I$

$$\Rightarrow \quad \log_{10} k = \log_{10} k_0 + (b_A + b_B - b_{AB})I$$

$$k = k_0 e^{b'I} \rightarrow k_0(1 + b'I) \qquad \text{weak linear dependence}$$

Pressure Dependence of Reaction Rates

From classical thermodynamics

$$dG = VdP - SdT \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V$$

For a reaction at equilibrium

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{1}{nRT}\left(\frac{\partial \Delta G}{\partial P}\right)_T = -\frac{\Delta \bar{V}^\circ}{RT}$$

$$\Delta \bar{V}^\circ = \bar{V}_{\text{prod}} - \bar{V}_{\text{react}} = \left(\bar{V}^\ddagger - \bar{V}_{\text{react}}\right) - \left(\bar{V}^\ddagger - \bar{V}_{\text{prod}}\right) = \Delta^\ddagger \bar{V}_1^\circ - \Delta^\ddagger \bar{V}_{-1}^\circ$$

Since $\qquad K = k_1 / k_{-1}$

$$\left(\frac{\partial \ln k_1}{\partial P}\right)_T - \left(\frac{\partial \ln k_{-1}}{\partial P}\right)_T = -\frac{\Delta^\ddagger \bar{V}_1^\circ}{RT} + \frac{\Delta^\ddagger \bar{V}_{-1}^\circ}{RT}$$

Most books state

$$\left(\frac{\partial \ln k_1}{\partial P}\right)_T = -\frac{\Delta^\ddagger \bar{V}_1^\circ}{RT} \qquad \left(\frac{\partial \ln k_{-1}}{\partial P}\right)_T = \frac{\Delta^\ddagger \bar{V}_{-1}^\circ}{RT}$$

This neglects the difference between K° and K_c only different for $\Delta \nu \neq 0$

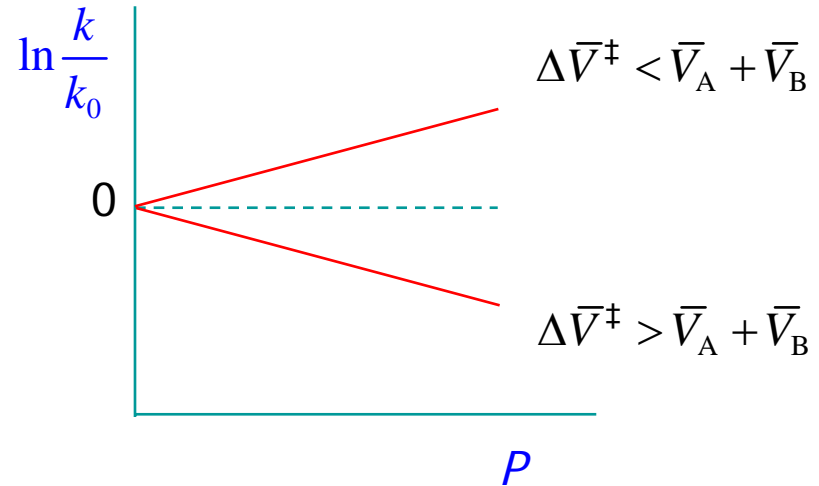Since $K_c = \bar{V}^\circ K^\circ$ for $\Delta \nu = -1$

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta^\ddagger \bar{V}^\circ}{RT} - \kappa_0 \qquad \longleftarrow \text{ volume of activation}$$

compressibility of the solvent $\qquad \left(\frac{\partial \ln V}{\partial P}\right)_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

Pressure Dependence – 2

Neglecting κ_0

$$\ln k = \ln k_0 - \frac{\Delta \overline{V}^{\ddagger}}{RT} P$$

$$\Delta \overline{V}^{\ddagger} < \overline{V}_A + \overline{V}_B$$

$$\Delta \overline{V}^{\ddagger} > \overline{V}_A + \overline{V}_B$$

If reactants..   expect

combine $\Delta \overline{V}^{\ddagger} < 0$

dissociate $\Delta \overline{V}^{\ddagger} > 0$

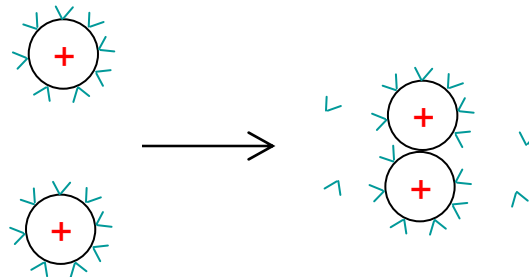have like charges $\Delta \overline{V}^{\ddagger} < 0$
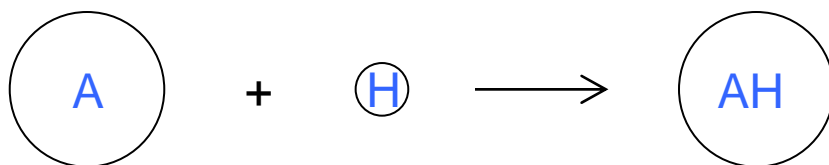
unlike charges $\Delta \overline{V}^{\ddagger} > 0$

similar effects for polar molecules (dipoles)
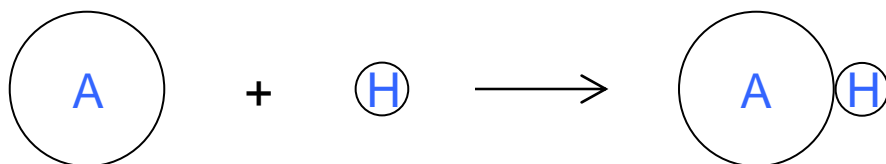Solvent effects are often dominant

Electrorestriction

ordering of the solvent
molecules reduces
their effective volume

Volume of Activation for H Atom Reactions

$$\Delta \overline{V}^{\ddagger} = \overline{V}_{AH} - \overline{V}_A - \overline{V}_H \approx -\overline{V}_H$$

$$\Delta \overline{V}^{\ddagger} \approx V_w \left(H \right) - \overline{V}_H$$

Comparison of $\Delta \overline{V}^{\ddagger}\left(H \right)$ and $\Delta \overline{V}^{\ddagger}\left(Mu \right)$ shows that V(Mu) > V(H) in water.