Exercises

1. Chose conditions such that ionic strength remains constant during a titration of a dye in acetate buffer.
2. Chose conditions such that ionic strength remains approximately constant during a titration of a dye in phosphate buffer (pH 7).
3. Derive the rate law for the enolization of a ketone.
4. Explain, why the ketonization rate of acetophenone enol saturates at pH ≈ 10.2.
5. Explain why the three mechanisms discussed for the "uncatalyzed" ketonization of acetophenone all give rise to rate laws that are independent of pH.
6. Give an example of upward curvature in a pH–rate profile that is due to a change in the reaction mechanism.
7. Give an example of downward curvature in a pH–rate profile that is due to a change in the rate-determining step.
8. Describe an experiment to determine the individual contributions to buffer catalysis by the general acid and the general base.
9. Explain why the rate of ketonization of phenol decreases above pH 10.
10. Give an upper limit for the acidity constant of phenylynol.
11. Why does the Bronsted parameter α increase with the standard free energy of reaction $\Delta_r G°$?
12. Estimate the rate constant (T = 298 K) for the acid-catalyzed ketonization of propen-2-ol k_{H^+} in water given that the enolization constant of acetone is $pK_E = 8.33$ and the acidity constant of protonated acetone is $pK_{a,c}^{K^+} = -3.06$.
13. Estimate the rate constant (T = 298 K) for the uncatalyzed ketonization of propen-2-ol k_{H^+} in water given that the enolization constant of acetone is $pK_E = 8.33$ and the acidity constant of propen-2-ol is $pK_{a,c}^{E} = 10.94$.
14. The acid-catalyzed rate constants for the ketonization of phenol (to 2,4-cyclohexadienone, measured by deuteration of phenol) and of the reverse reaction are $k_{H^+}^{K} = 1.0 \times 10^{-7}\ M^{-1}\ s^{-1}$ and $k_{H^+}^{E} = 5.4 \times 10^{5}\ M^{-1}\ s^{-1}$. The acidity constant of phenol is $pK_{a,c}^{E} = 9.84$. Calculate the acidity constant of 2,4-cyclohexadienone as a carbon acid.