Key for Take-Home Assignment 1
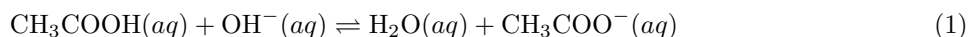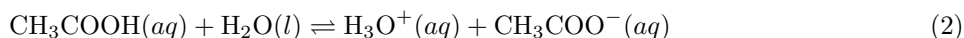
When acetic acid, CH_3COOH, reacts with a strong base, which is a source of hydroxide ion, OH^-, the reaction is

$$CH_3COOH(aq) + OH^-(aq) \rightleftharpoons H_2O(aq) + CH_3COO^-(aq) \tag{1}$$

We can divide Reaction 1 into two steps: an acid dissociation reaction, in which acetic acid donates a proton to water

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \tag{2}$$

and a neutralization reaction, in which the H_3O^+ from Reaction 2 reacts with the strong base

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l) \tag{3}$$

Answer the following prompts about this system:

1. Write the equilibrium constant expressions for Reactions 1–3 and report the value of the equilibrium constant for each reaction. What do these values suggest to you about the relative favorability of these reactions?

   The equilibrium constant expressions and equilibrium constants for the three reactions are

   $$K_{\text{rxn 1}} = \frac{[CH_3COO^-]}{[CH_3COOH][OH^-]} = \frac{1}{K_b} = \frac{K_a}{K_w} = \frac{1.8 \times 10^{-5}}{1.00 \times 10^{-14}} = 1.8 \times 10^9$$

   $$K_{\text{rxn 2}} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = K_a = 1.8 \times 10^{-5}$$

   $$K_{\text{rxn 3}} = \frac{1}{[H_3O^+][OH^-]} = \frac{1}{K_w} = \frac{1}{1.00 \times 10^{-14}} = 1.00 \times 10^{14}$$

   For reaction (1), note that it is the reverse of the base dissociation reaction for CH_3COO^-, which explains why the equilibrium constant for reaction (1) is $(K_b)^{-1}$. Recall, as well, that $K_a \times K_b = K_w$ where K_a is the acid dissociation constant for acetic acid.

   From the equilibrium constants, we see that reaction (1) and reaction (3) essentially go to completion as they have very large values of K, which makes sense as reaction (1) is between a weak acid and a strong base and reaction (3) is between a strong acid and a strong base; however, reaction (2) does not take place to any appreciable extent, which is consistent with our understanding of what it means to be a weak acid.

2. Using your answers to Question 1, what are the value of ΔG° for Reactions 1–3? What do these values suggest to you about the relative favorability of these reactions?

   We know that $\Delta G^\circ = -RT\ln K$, where R is the gas constant and T is the temperature in Kelvin. As the temperature is not given, we will assume that it is 25°C, or 298 K. The values are

   $$\Delta G^\circ_{\text{rxn 1}} = -(8.314 \text{ J/mol}_{\text{rxn}} \bullet \text{K})(298 \text{ K})\ln(1.8 \times 10^9) = -52800 \text{ J/mol}_{\text{rxn}} \rightarrow -52.8 \text{ kJ/mol}_{\text{rxn}}$$

   $$\Delta G^\circ_{\text{rxn 2}} = -(8.314 \text{ J/mol}_{\text{rxn}} \bullet \text{K})(298 \text{ K})\ln(1.8 \times 10^{-5}) = 27,100 \text{ J/mol}_{\text{rxn}} \rightarrow 27.1 \text{ kJ/mol}_{\text{rxn}}$$

   $$\Delta G^\circ_{\text{rxn 3}} = -(8.314 \text{ J/mol}_{\text{rxn}} \bullet \text{K})(298 \text{ K})\ln(1.0 \times 10^{14}) = -79900 \text{ J/mol}_{\text{rxn}} \rightarrow -79.9 \text{ kJ/mol}_{\text{rxn}}$$

Reaction (1) has a large negative value for $\Delta G°$, which is consistent with our observation from the previous question that the reaction of a weak acid with a strong base essentially goes to completion; the same is true for reaction (3). The postive $\Delta G°$ for reaction (2) is consistent with our observation that a weak acid does not dissociate to any appreciable extent in water.

3. The change in enthalpy, $\Delta H°$, for Reaction 3 is reported as -57.1 kJ/mol$_{\text{rxn}}$ at a temperature of 298 K, and, at least in principle, is independent of the specific acid or base. If the change in enthalpy for Reaction 1 is -55.9 kJ/mol$_{\text{rxn}}$, as has been reported, then what is $\Delta H°$ for Reaction 2? Explain why the $\Delta H°$ for Reaction 2 is so different from the $\Delta H°$ values for Reaction 1 and Reaction 3.

Reaction (1) is the sum of reaction (2) and reaction (3); thus

$$\Delta H°_{\text{rxn 2}} = \Delta H°_{\text{rxn 1}} - \Delta H°_{\text{rxn 3}} = -55.9 \text{ kJ/mol}_{\text{rxn}} - (-57.1 \text{ kJ/mol}_{\text{rxn}}) = 1.2 \text{ kJ/mol}_{\text{rxn}}$$

A reaction's change in enthalpy is negative when weaker bonds break and when stronger bonds form, and it is positive when stronger bonds break and when weaker bonds forms. When we compare reaction (1) to reaction (2), we see that in each case we break the same bond—the OH bond in acetic acid–so this cannot account for the difference in their respective $\Delta H°$ values; however, in reaction (1) the OH bond formed in H_2O is much stronger than the OH bond formed in H_3O^+; thus, the much less negative (indeed, the positive) $\Delta H°$ for reaction (2) is not surprising.

4. What is the change in entropy, $\Delta S°$, for Reaction 2?

We know that $\Delta G°_{\text{rxn 2}} = \Delta H°_{\text{rxn 2}} - T\Delta S°_{\text{rxn 2}}$; thus

$$\Delta S°_{\text{rxn 2}} = \frac{\Delta H°_{\text{rxn 2}} - \Delta G°_{\text{rxn 2}}}{T}$$

$$\Delta S°_{\text{rxn 2}} = \frac{1.2 \text{ kJ/mol}_{\text{rxn}} - 27.1 \text{ kJ/mol}_{\text{rxn}}}{298 \text{ K}} = -0.0869 \text{ kJ/Kmol}_{\text{rxn}} \rightarrow -86.9 \text{ J/Kmol}_{\text{rxn}}$$

5. What is the expected value for acetic acid's acid dissociation constant, K_a at a temperature of 323 K? Is acetic acid a *stronger* weak acid or a *weaker* weak acid at higher temperatures?

The relationship between K and temperature is given by the following equation

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

Substituting in known values and solving for K gives

$$\ln K = -\frac{1.2 \text{ kJ/mol}_{\text{rxn}}}{(8.314 \times 10^{-3} \text{ kJ/mol} \bullet \text{K})(323 \text{ K})} + \frac{-0.0869 \text{ kJ/Kmol}_{\text{rxn}}}{8.314 \times 10^{-3} \text{ kJ/mol} \bullet \text{K}} = -10.899$$

$$K = 1.87 \times 10^{-5}$$

As expected for an endothermic reaction, the reaction's equilibrium constant increases at higher temperatures; thus, acetic acid is a stronger weak acid at higher temperatures than it is at lower temperatures.