

Practice problems for thermodynamics

KEY

- 1) The dissociation of acetic acid has an equilibrium constant of  $1.75 \times 10^{-5}$  at  $25^\circ\text{C}$ . What is the standard free energy change for this process at  $25^\circ\text{C}$ ?

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$\Delta G^\circ = -(8.3145 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298\text{K}) \ln(1.75 \times 10^{-5})$$

$$\Delta G^\circ = 27100 \text{ J/mol} = 27.1 \text{ kJ/mol}$$

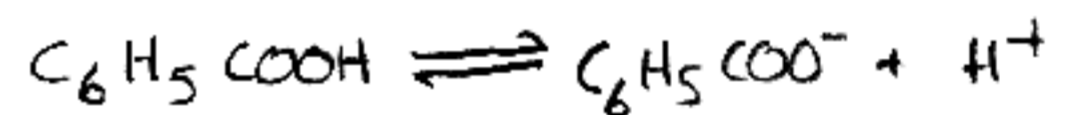
- 2) The standard free energy change for the dissociation of benzoic acid is  $23.97 \text{ kJ/mol}$ . What is the equilibrium constant at  $25^\circ\text{C}$ ?

$$K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$$

$$K_{eq} = e^{-\left[\frac{23970 \frac{\text{J}}{\text{mol}}}{(8.3145 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298\text{K})}\right]}$$

$$K_{eq} = 6.29 \times 10^{-5}$$

- 3) The standard free energy change for the dissociation of benzoic acid is  $23.97 \text{ kJ/mol}$ . What is the free energy change at  $25^\circ\text{C}$  if the concentration of benzoic acid is  $0.105 \text{ M}$ , the concentration of the benzoate ion is  $1.05 \times 10^{-6} \text{ M}$ , and the pH is  $6.903$ ?



$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = 23970 \frac{\text{J}}{\text{mol}} + (8.3145 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298\text{K}) \ln \frac{(1.05 \times 10^{-6})(1.25 \times 10^{-7})}{(0.105)}$$

$$\Delta G = -43.9 \text{ kJ/mol}$$

$$\text{pH} = -\log[\text{H}^+]$$

$$[\text{H}^+] = 10^{-\text{pH}}$$

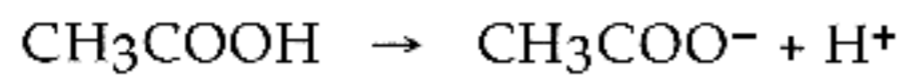
$$[\text{H}^+] = 1.25 \times 10^{-7} \text{ M}$$

- 4) The conversion of glucose-1-phosphate to glucose-6-phosphate by the enzyme phosphoglucomutase has a standard free energy change of  $-7.60 \text{ kJ/mol}$ . Calculate the equilibrium constant for this reaction at  $25^\circ\text{C}$ .

$$K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$$

$$K_{eq} = 21.5$$

5) Acetic acid dissociates in water according to the following equation:



At equilibrium, the pH was found to be 3.377,  $[\text{CH}_3\text{COO}^-] = 4.20 \times 10^2 \mu\text{M}$  and  $[\text{CH}_3\text{COOH}] = 10.0 \text{ mM}$ . What are  $\Delta G^\circ$  and  $\Delta G$  at 25 °C?

$\Delta G$  IS ZERO SINCE WE ARE AT EQUILIBRIUM

TO GET  $\Delta G^\circ$  WE NEED  $K_{eq}$ :

$$K_{eq} = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$[\text{H}^+] = 10^{-\text{pH}}$   
 $= 4.20 \times 10^{-4} \text{ M}$

$[\text{CH}_3\text{COO}^-] = 4.20 \times 10^2 \mu\text{M} \times \frac{10^{-6} \text{ M}}{\mu\text{M}} = 4.20 \times 10^{-4} \text{ M}$

$[\text{CH}_3\text{COOH}] = 10.0 \text{ mM} \times \frac{10^{-3} \text{ M}}{\text{mM}} = 1.00 \times 10^{-2} \text{ M}$

$K_{eq} = 1.76 \times 10^{-5}$

$\Delta G^\circ = -RT \ln K_{eq}$

$\Delta G^\circ = 27.1 \text{ kJ/mol}$

6) In an *E. coli* cell, the concentrations of ATP, ADP and inorganic phosphate might be 7.90 mM, 1.04 mM and 7.9 mM, respectively. Given that the hydrolysis of ATP has a standard free energy change taken at pH 7.0 ( $\Delta G^\circ$ ) of -30.0 kJ/mol, what is the standard free energy change,  $\Delta G^\circ$ , for this hydrolysis reaction (pH 0)? Calculate the free energy change,  $\Delta G$ , for this reaction in the cell at 37.0 °C and buffered at pH 7.0.

The hydrolysis of ATP:



PURE LIQUID → STANDARD STATE, ACTIVITY = 1  
 (LEAVE OUT OF "Q")

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{ADP}^{3-}][\text{HPO}_4^{2-}][\text{H}^+]}{[\text{ATP}^{4-}]} \Rightarrow \Delta G = \Delta G^\circ + RT \ln \frac{[\text{ADP}^{3-}][\text{HPO}_4^{2-}]}{[\text{ATP}^{4-}]} + RT \ln [\text{H}^+]$$

COMBINE TO GET  $\Delta G^{\circ'}$

$\Delta G^{\circ'} = \Delta G^\circ + RT \ln [\text{H}^+]$

$\Delta G^\circ = \Delta G^{\circ'} - RT \ln [\text{H}^+]$

$\Delta G^\circ = -3.00 \times 10^4 \text{ J/mol} - (8.3145 \frac{\text{J}}{\text{mol K}})(298 \text{ K}) \ln (1.0 \times 10^{-7})$

$\Delta G^\circ = 9.9 \text{ kJ/mol}$  ← NOTICE VERY DIFFERENT AT pH 0!

$$\Delta G = \Delta G^{\circ'} + RT \ln \frac{[\text{ADP}^{3-}][\text{HPO}_4^{2-}]}{[\text{ATP}^{4-}]} \Rightarrow \Delta G = -47.7 \text{ kJ/mol}$$

$\Delta G^{\circ'}$  ← -30.0 kJ/mol  
 $RT$  ← 310 K

↑ HYD. IS VERY SPONT. UNDER THESE CONDS.

7) What is the biochemical significance of the equation  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ ?

$\Delta S_{\text{univ}} \Rightarrow$  MUST BE POSITIVE FOR A PROCESS TO  
BE SPONTANEOUS

$\Delta S_{\text{sys}} \Rightarrow$  BIOCHEMICAL SYSTEMS ARE MORE ORDERED  
THAN THE ENVIRONMENT THEY AROSE FROM,  
 $\Delta S_{\text{sys}}$  IS THEREFORE NEGATIVE

$\Delta S_{\text{surr}} \Rightarrow$  MUST THEREFORE BE POSITIVE & HAVE A  
LARGER MAGNITUDE THAN  $\Delta S_{\text{sys}}$ , MORE  
DISORDER WAS INTRODUCED TO THE SURROUNDINGS  
THAN ORDER WAS INTRODUCED TO THE SYSTEM.

OVERALL, DISORDER INCREASES ( $\Delta S_{\text{univ}} > 0$ )  
ALLOWS FOR THE FORMATION OF COMPLEX &  
ORDERED SYSTEMS NECESSARY FOR LIFE.