

SOLUTIONS TO PROBLEMS

Chapter 1

1. An amino or imino group gives a molecule a positive charge; a carboxylate or phosphoryl group gives a molecule a negative charge.
2. **A** Thiol (sulfhydryl) group
B Carbonyl group
C Amide linkage
D Phosphoanhydride (pyrophosphoryl) linkage
E Phosphoryl group (P_i)
F Hydroxyl group
3. Hydrolysis reactions tend to occur with an increase in entropy, because the highly ordered polymer is broken down into separate units.
4. Typical prokaryotic cells are 1–10 μm in diameter, so *T. acidophilus* is about 10–300 times larger (or has 1000 to 27 million times the volume). Typical eukaryotic cells are 10–100 μm in diameter, so *T. acidophilus* is about the same size or up to 30 times larger (or has the same to 27,000 times the volume).
5. The data indicate that eukaryotes are more similar to the archaea than to the eubacteria.
6. (a) Liquid water; (b) ice has less entropy at the lower temperature.
7. (a) Decreases; (b) increases; (c) increases; (d) no change.
8. No. When the change in enthalpy is positive and the change in entropy is negative, the free energy change for the process is greater than zero, which makes the process unfavorable.
9. (a) False. A spontaneous reaction occurs in only one direction.
(b) False. Thermodynamics does not specify the rate of a reaction.
(c) True. (d) True. A reaction is spontaneous as long as $\Delta S > \Delta H/T$.
10. (a) $T = 273 + 10 = 283 \text{ K}$
 $\Delta G = \Delta H - T\Delta S$
 $\Delta G = 15 \text{ kJ} - (283 \text{ K})(0.05 \text{ kJ} \cdot \text{K}^{-1})$
 $= 15 - 14.15 \text{ kJ} = 0.85 \text{ kJ}$
 ΔG is greater than zero, so the reaction is not spontaneous.
(b) $T = 273 + 80 = 353 \text{ K}$
 $\Delta G = \Delta H - T\Delta S$
 $\Delta G = 15 \text{ kJ} - (353 \text{ K})(0.05 \text{ kJ} \cdot \text{K}^{-1})$
 $= 15 - 17.65 \text{ kJ} = -2.65 \text{ kJ}$
 ΔG is less than zero, so the reaction is spontaneous.
11. $\Delta G = \Delta H - T\Delta S$
 $\Delta G = -7000 \text{ J} \cdot \text{mol}^{-1} - (298 \text{ K})(-25 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
 $\Delta G = -7000 + 7450 \text{ J} \cdot \text{mol}^{-1} = 450 \text{ J} \cdot \text{mol}^{-1}$
The reaction is not spontaneous because $\Delta G > 0$. The temperature must be decreased in order to decrease the value of the $T\Delta S$ term.
12. $\Delta G^{\circ} = -RT \ln \frac{[C]}{[A][B]}$
 $= -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K}) \ln \frac{(0.009)}{(0.002)(0.003)}$
 $= -18,000 \text{ J} \cdot \text{mol}^{-1} = -18 \text{ kJ} \cdot \text{mol}^{-1}$
13. $\Delta G^{\circ} = -RT \ln K_{eq} = -RT \ln \frac{[C][D]}{[A][B]}$
 $= -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K}) \ln \frac{(3 \times 10^{-3})(5 \times 10^{-3})}{(10 \times 10^{-3})(15 \times 10^{-3})}$
 $= 5700 \text{ J} \cdot \text{mol}^{-1} = 5.7 \text{ kJ} \cdot \text{mol}^{-1}$

Since ΔG° is positive, the reaction is endergonic under standard conditions.

14. $K_{eq} = e^{-\Delta G^{\circ}/RT} = e^{-(-20,000 \text{ J} \cdot \text{mol}^{-1})/(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}$
 $= 4.6 \times 10^3$
15. From Eq. 1-17, $K_{eq} = [\text{G6P}]/[\text{G1P}] = e^{-\Delta G^{\circ}/RT}$
 $[\text{G6P}]/[\text{G1P}] = e^{-(-7100 \text{ J} \cdot \text{mol}^{-1})/(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}$
 $[\text{G6P}]/[\text{G1P}] = 17.6$
 $[\text{G1P}]/[\text{G6P}] = 0.057$
16. The cell membrane must be semipermeable so that the cell can retain essential compounds while allowing nutrients to enter and wastes to exit.
17. Membrane-enclosed cellular compartments are typical of eukaryotic but not prokaryotic cells.
18. Concentration = (number of moles)/(volume)
Volume = $(4/3)\pi r^3 = (4/3)\pi(5 \times 10^{-7} \text{ m})^3$
 $= 5.24 \times 10^{-22} \text{ m}^3 = 5.24 \times 10^{-16} \text{ L}$
Moles of protein = (2 molecules)/(6.022 $\times 10^{23}$ molecules $\cdot \text{mol}^{-1}$)
 $= 3.32 \times 10^{-24} \text{ mol}$
Concentration = $(3.32 \times 10^{-24} \text{ mol})/(5.24 \times 10^{-16} \text{ L})$
 $= 6.3 \times 10^{-9} \text{ M} = 6.3 \text{ nM}$
19. Number of molecules = (molar conc.)(volume) $(6.022 \times 10^{23} \text{ molecules} \cdot \text{mol}^{-1})$
 $= (1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1})(5.24 \times 10^{-16} \text{ L})$
 $(6.022 \times 10^{23} \text{ molecules} \cdot \text{mol}^{-1})$
 $= 3.2 \times 10^2 \text{ molecules}$
20. In order for ΔG to have a negative value (a spontaneous reaction), $T\Delta S$ must be greater than ΔH .
 $T\Delta S > \Delta H$
 $T > \Delta H/\Delta S$
 $T > 7000 \text{ J} \cdot \text{mol}^{-1}/(20 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
 $T > 350 \text{ K}$ or 77°C
21. (a) Because $K_{eq} = \frac{[R]}{[Q]} = 25$, at equilibrium, the concentration of R is 25 times greater than the concentration of Q. When equal concentrations of Q and R are mixed, molecules of Q will be converted to molecules of R.
(b) Let x = amount of Q converted to R, so that [R] will be $50 \mu\text{M} + x$ and [Q] will be $50 \mu\text{M} - x$. Since $K_{eq} = \frac{[R]}{[Q]} = 25$,
$$\frac{50 + x}{50 - x} = 25(50 - x)$$

$$50 + x = 1250 - 25x$$

$$26x = 1200$$

$$x = 46.15$$

$$[R] = 50 \mu\text{M} + 46.15 \mu\text{M} = 96.15 \mu\text{M}$$

$$[Q] = 50 \mu\text{M} - 46.15 \mu\text{M} = 3.85 \mu\text{M}$$
22. At $10^{\circ}\text{C} = 283 \text{ K}$ ($1/T = 0.00353$), $K_{eq} = 100$ and $\ln K = 4.61$.
At $30^{\circ}\text{C} = 303 \text{ K}$ ($1/T = 0.00330$), $K_{eq} = 10$ and $\ln K = 2.30$.
These two points generate a line on a van't Hoff plot ($\ln K_{eq}$ versus $1/T$) with a positive slope that is equal to $(-\Delta H^{\circ}/R)$. ΔH° must therefore be negative, indicating that enthalpy decreases during the reaction (heat is given off).

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Donald Voet



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