1. b (see scale drawings from the first lecture)
2. a. True. To maximize H-bonding when next to a non-polar solute, water gives up its rotational freedom (reducing its entropy)
   b. False. The stronger an acid, the <u>lower</u> its pK_a, or the stronger a <u>base</u>, the higher its pK_a.
   c. True
   d. True. Water can act as both an acid and a base.
   e. True. The higher the boiling point, the more cohesive the liquid (the stronger the interactions are between liquid molecules/atoms).
   f. False. A weak base is predominately <u>deprotonated</u> at pH's above its pK_a, and predominately protonated at pH's <u>below</u> its pK_a.
   g. False. If too dilute, a buffer cannot pick up or release enough protons to maintain the desired pH.
3. a
4. Many of these properties help stabilize environmental conditions, which gives time for organisms to arise and evolve (there may also be additional correct answers):
   High heat capacity – buffers earth's temperature, generating a more stable environment for the development of life
   Large heat of fusion – helps provide stability of temperature and state (liquid)
   Large heat of vaporization – helps provide stability of temperature and state; also allows for efficient cooling by animals that sweat
   Large liquid range – provides stability of state
   Solid is less dense than liquid – helps keep large bodies of water liquid by insulating water below (providing stability of state)
   High polarity – allows dissolution of a diversity of molecules and ions, providing for great chemical diversity
   High surface tension – exploited by some organisms, e.g. in plants, where water is transported by capillary action; also by insects that move around on the surface of water
5. a. HB
   b. HB
   c. HA
   d. pH 3: HA, HB; pH 4: [HA]=[A⁻], HB; pH 7: A⁻, B⁻
   e. pH 4: $\frac{[A^-]}{[HA]} = 10^{pH-pKa} = 10^{4-4} = 10^0 = \frac{1}{1}$; $\frac{[B^-]}{[HB]} = 10^{pH-pKa} = 10^{4-6} = 10^{-2} = \frac{1}{100}$

   pH 7: $\frac{[A^-]}{[HA]} = 10^{pH-pKa} = 10^{7-4} = 10^3 = \frac{1000}{1}$; $\frac{[B^-]}{[HB]} = 10^{pH-pKa} = 10^{7-6} = 10^1 = \frac{10}{1}$

   f. From part e, at pH 4 $\frac{[A^-]}{[HA]} = \frac{1}{1}$, so the fraction protonated, $\frac{[HA]}{[HA]+[A^-]} = \frac{1}{1+1} = \frac{1}{2}$ (= 0.5)

   At pH 4 $\frac{[B^-]}{[HB]} = \frac{1}{100}$, so the fraction protonated, $\frac{[HB]}{[HB]+[B^-]} = \frac{100}{100+1} = \frac{100}{101}$ (= 1)

   At pH 7 $\frac{[A^-]}{[HA]} = \frac{1000}{1}$, so the fraction protonated, $\frac{[HA]}{[HA]+[A^-]} = \frac{1}{1+1000} = \frac{1}{1001}$ (= 0.001)

   At pH 7 $\frac{[B^-]}{[HB]} = \frac{10}{1}$, so the fraction protonated, $\frac{[HB]}{[HB]+[B^-]} = \frac{1}{1+10} = \frac{1}{11}$ (= 0.09)

   g. For HA and HB, respectively, at pH 3: 0, 0; at pH 4: none ([0] = [-1]), 0; at pH 7, -1, -1
   h. Since both are charged when deprotonated, the fraction charged at pH 4 and pH 7 will equal one minus the fraction protonated (calculated in part f):

$$\frac{[HA]}{[HA]+[A^-]} + \frac{[A^-]}{[HA]+[A^-]} = 1 \text{ , so the fraction charged, } \frac{[A^-]}{[HA]+[A^-]} = 1 - \frac{[HA]}{[HA]+[A^-]}$$

At pH 4, $\frac{[A^-]}{[HA]+[A^-]} = 1 - \frac{1}{2} = \frac{1}{2}$ $(= 0.5)$ and $\frac{[B^-]}{[HB]+[B^-]} = 1 - \frac{100}{101} = \frac{1}{101}$ $(= 0.01)$

At pH 7, $\frac{[A^-]}{[HA]+[A^-]} = 1 - \frac{1}{1001} = \frac{1000}{1001}$ $(= 1)$ and $\frac{[B^-]}{[HB]+[B^-]} = 1 - \frac{1}{11} = \frac{10}{11}$ $(= 0.9)$

 i. The average charge is the fraction charged multiplied by the value of the charge:
  At pH 4, the average charge on HA is: $0.5 \times (-1) = \mathbf{-0.5}$
  At pH 4, the average charge on HB is: $0.01 \times (-1) = \mathbf{-0.01}$
  At pH 7, the average charge on HA is: $1 \times (-1) = \mathbf{-1}$
  At pH 7, the average charge on HB is: $0.9 \times (-1) = \mathbf{-0.9}$

 j. For HA, $pH = pK_a + log\frac{[A^-]}{[HA]} = 4 + log\frac{1}{3} = 4 - 0.48 = \mathbf{3.52}$

  For HB, $pH = pK_a + log\frac{[B^-]}{[HB]} = 6 + log\frac{1}{3} = 6 - 0.48 = \mathbf{5.52}$

 k. For HA, 25% deprotonated, $pH = pK_a + log\frac{[A^-]}{[HA]} = 4 + log\frac{25\%}{75\%} = 4 - 0.48 = \mathbf{3.52}$

  For HA, 10% deprotonated, $pH = pK_a + log\frac{[A^-]}{[HA]} = 4 + log\frac{10\%}{90\%} = 4 - 0.95 = \mathbf{3.05}$

  For HA, 1% deprotonated, $pH = pK_a + log\frac{[A^-]}{[HA]} = 4 + log\frac{1\%}{99\%} = 4 - 2.00 = \mathbf{2.00}$

  For HB, 25% deprotonated $pH = pK_a + log\frac{[B^-]}{[HB]} = 6 + log\frac{25\%}{75\%} = 6 - 0.48 = \mathbf{5.52}$

  For HB, 10% deprotonated, $pH = pK_a + log\frac{[B^-]}{[HB]} = 6 + log\frac{10\%}{90\%} = 6 - 0.95 = \mathbf{5.05}$

  For HB, 1% deprotonated, $pH = pK_a + log\frac{[B^-]}{[HB]} = 6 + log\frac{1\%}{99\%} = 6 - 2.00 = \mathbf{4.00}$

 l. For HA, pH < 4; for HB, pH < 6
 m. Average charge of -0.8 means 0.8 (or 8/10 or 80%) have -1 charge and 0.2 (or 2/10 or 20%) have no charge:

  For HA, $pH = pK_a + log\frac{[A^-]}{[HA]} = 4 + log\frac{80\%}{20\%} = 4 + 0.60 = \mathbf{4.60}$

  For HB, $pH = pK_a + log\frac{[B^-]}{[HB]} = 6 + log\frac{80\%}{20\%} = 6 + 0.60 = \mathbf{6.60}$

 n. HA: pH 3-5; HB: pH 5-7
 o. Neither; both would be equally limited at pH 5. The only difference would be that HA would be better able to resist decreases in pH, and HB would be better able to resist increases in pH.

6. $pH = pK_a + log\frac{[A^-]}{[HA]} = 5.9 + log\frac{0.0999}{0.0001} = 5.9 + 3 = \mathbf{8.9}$

7. a. HCl. Cl^- is more stable than F^- because of its larger radius.
 b. Cysteine's -SH. S^- is more stable than O^- because of its larger radius.
 c. Tyrosine's -OH. Tyrosine's ring provides resonance stabilization to the O^- (delocalizes negative charge).
 d. Lysine's $-NH_3^+$. Resonance in the guanidino group of Arg stabilizes the protonated structure (delocalizes positive charge).

8. a. A
 b. No; pH 5 is far from the pKa's of alanine's ionizable groups (pKa 2 and 9.5). Alanine would be able to buffer from pH 1-3 and 8.5-10.5 (with pH 2 and 9.5 being best)

9. (Since there are 20 standard aa's, there are 6 of the 26 letters that are not used): B, J, O, U, X, Z.