1. (10 pts) Ammonium nitrate, $\text{NH}_4\text{NO}_3$, is synthesized from ammonia ($\text{NH}_3$) and nitric acid. Do you expect the pH of an ammonium nitrate solution to be $< 7$ or $> 7$ (circle one)? The $pK_b$ of ammonia is 4.75. Write down the equilibrium to which this $pK_b$ refers. Is $\text{NH}_4^+$ a weak acid, strong acid, weak base, or strong base (circle one)? What is its $pK_a$?
The enzyme lactate dehydrogenase is essential to the maintenance of anaerobic metabolism. The proposed reaction mechanism for the conversion of pyruvate to lactate is shown here, along with a graph of the pH dependence of enzymatic activity. Typical approximate \( pK_a \)s for amino acid side chains are Arg 12.5, His 6, Asp 4.

(a; 6 pts) Based on the mechanism shown, explain why the activity drops off as pH increases.

(b; 6 pts) At pH 7 the enzyme is 50\% as active as it is at pH 5 or below. This has been interpreted as meaning that there is a residue with a \( pK_a \) of 7 that is important for catalysis. In terms of one of the equations given on the front page of this exam, what is the basis for this measurement of the \( pK_a \)?
(c; 4 pts) The presence of the Asp168 nearby was thought to raise the pKₐ of His195-H⁺ from its normal 6 to about 7. Explain why it should have this effect. [In 1988, the Asp168 was mutated to Ala (an uncharged residue). Surprisingly, there was no effect on pKa. It took 20 years for the suggestion to emerge that a Glu residue swings in to replace the Asp168 in the mutant.]

3. The sketch below shows three possible microstates for gases bouncing around in boxes. Each box has the same total kinetic energy.

(a; 8 pts) Which box (circle it) looks like it has a Boltzmann distribution of speeds? How do you know? Why is the microstate on the left a member of a configuration that is much less likely than the predominant configuration?
(b; 6 pts) What is the fundamental basis of the derivation of the Boltzmann distribution? (No equations, just a sentence or two).

4. Consider trusting to luck playing poker
   (a; 8 pts) Calculate the number of ways \( W_4 \) to draw a four of a kind in 5-card stud. (i.e. you are dealt 5 cards from a deck of 52 cards). Calculate the number of ways \( W_{SF} \) to draw a straight flush, assuming that an ace can only be a high card (i.e. Ace-2-3-4-5 does not count as a straight).

   (b; 4 pts) If the total possible number of 5-card stud hands is 2598960, what is the total probability of drawing either a four of a kind or a straight flush?
5. (8 pts) Thermodynamics. Consider the Gibbs free energy \( G = H - TS \). We have shown that the inequality \( \Delta G = \Delta H - T \Delta S < 0 \) holds for any spontaneous process. In terms of the 2nd Law of Thermodynamics, why does \( \Delta H < 0 \) help drive the process forward? What is one main advantage of using free energy rather than \( \Delta S - q/T > 0 \) as our routine computational criterion for spontaneity?

6. Consider a titration of 100 ml of 0.125 M formic acid (HCOOH), pKa = 3.75, with 0.125 M NaOH.
   (a; 15 pts) Upon addition of 80 ml of the NaOH, use the H-H relationship to calculate the \([H^+]\), pH (give pH to 4 significant figures), \([HCOOH]\), and \([HCOO^-]\), and also calculate \([HO^-]\). To apply the H-H in this way, what must be true about \([HCOOH]\), and \([HCOO^-]\)?
(b; 8 pts) Assuming that the same 80 ml of added NaOH initially neutralizes some of the HCOOH and then some of the resulting HCOO- reassociates with protons via HCOOH $\leftrightarrow$ HCOO$^-$ + H$^+$, calculate the pH to 4 significant figures. Why is it different from your answer in (a)?

7. (5 pts) Given the equilibria below, what is the value for the last equilibrium constant in terms of all the others?

$$
A + 2 B \leftrightarrow C + D \quad K_1
$$

$$
B \leftrightarrow E \quad K_2
$$

$$
C \leftrightarrow E + F \quad K_3
$$

$$
A + B \leftrightarrow D + F \quad K_{eq} = \text{___________________________}
$$
8. (12 pts) Consider the reversible carbamylation of the N-terminus of Hb with carbon dioxide and also the binding of oxygen to hemoglobin. Reversible carbamylation of the N-terminus of Hb occurs much more readily ($K_1 \gg K_3$) on deoxygenated hemoglobin. Fill in the box on the linked equilibria below and explain how $O_2$ binding in the lungs helps drive off $CO_2$. 

\[
\begin{align*}
\text{Carbamylation equilibria} & \\
\text{Oxygenation equilibria} & \\
\text{Hb} + O_2 + CO_2 & \rightleftharpoons Hb - CO_2 + O_2 \\
\text{Hb} \cdot O_2 - CO_2 & \rightleftharpoons Hb - CO_2 + O_2
\end{align*}
\]