The insert contains important data. You may use the reverse for scratch work but enter **ALL** work to be graded in the space provided with each question. Show your work in all questions involving a calculation in order to receive credit. The temperature is 25ºC and the solvent is water in all problems involving ionic equilibria.

1) (20 points) A 100 Liter flask at 0ºC contains gaseous hydrogen, nitrogen, and ammonia; 10 mL of liquid ammonia; and a solid catalyst for the exothermic reaction $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$. Initially all species are at equilibrium. What is the effect on the equilibrium partial pressure of nitrogen as a result of the following changes? (Enter + for an increase in p_{N2}; -, for a decrease; 0, for no change.)

Alteration of the system	effect on p_{N2}
a) add additional gaseous hydrogen	_-_(decrease)____
b) add gaseous helium	_0 (no change)___
c) add 1.0 mL of liquid ammonia	_0 (no change)___
d) increase the temperature	_+_(increase)____

The equilibrium expression for the reaction is $K_p = p_{NH3}^2/(p_{H2}^3 p_{N2})$.

a) An increase in p_{H2} leads to the formation of additional ammonia and consumption of nitrogen.

b) Helium is neither a reactant nor a product so its partial pressure has no effect on the position of the equilibrium.

c) The flask contained liquid ammonia prior to the addition of more ammonia. The equilibrium between liquid and gaseous ammonia, i.e. $NH_3(l) \rightarrow NH_3(g)$, leads to the equilibrium expression $K_{vp} = p_{NH3}$. K_{vp} and therefore p_{NH3} are constant if the temperature is fixed. Adding additional liquid ammonia has no effect on the position of equilibrium.

d) An increase in temperature applies a stress to the system which is relieved by a shift of the equilibrium to the left.

2) (45 points) This problem deals with a 0.50 M solution of the base ethylamine, $CH_3CH_2NH_2$. The pK_a of its conjugate acid, $CH_3CH_2NH_3^+$, is 10.68.

a) Determine the value of the equilibrium constant for the reaction
$CH_3CH_2NH_2(aq) + H_3O^+(aq) \rightarrow CH_3CH_2NH_3^+(aq) + H_2O(l)$

The reaction is the reverse of the reaction which defines Ka, namely
$CH_3CH_2NH_3^+(aq) + H_2O(l) \rightarrow CH_3CH_2NH_2(aq) + H_3O^+(aq)$.
The equilibrium constant for the reaction is the inverse of Ka:
$K = 1/K_a = 1/10^{-pKa} = 10^{pKa} = 10^{10.68} = 4.8 \times 10^{10}$.

b) Calculate the pH of the solution.

The problem requests the pH of a 0.50 M aqueous solution of the base ethylamine. **This is a pure base problem.** The relevant reaction is
$CH_3CH_2NH_2(aq) + H_2O(l) \rightarrow CH_3CH_2NH_3^+(aq) + OH^-(aq)$
For which $K_b = [CH_3CH_2NH_3^+][OH-]/[CH_3CH_2NH_2]$ (eqn 1).

$K_b = K_w/K_a = (1.0 \times 10^{-14})/(10^{-10.68}) = 4.8 \times 10^{-4} << 1$.
We have a weak base but not a very weak base. Therefore,
$[CH_3CH_2NH_3^+] = [OH-]$ and $[CH_3CH_2NH_2]_0 \approx [CH_3CH_2NH_2]$.
Equation (1) simplifies to $4.8 \times 10^{-4} = [OH-]2/(0.5\ M)$, a result which yields $[OH^-] = 0.015$ M. The $pOH = -\log_{10}[OH^-] = 1.81$ and the pH = 14.00 – pOH is 12.19.

3) (45 points) The task in this problem is the preparation of a pH 7.00 buffer.

a) The insert provides a list of acids and their pK_a's. Select the acid best suited for the preparation of the buffer. Provide the basis for your selection.

The best choice is dihydrogen phosphate whose pK_a, 7.21, lies closest to the target pH.

b) Suppose that you are provided a 0.10 M solution of the acid selected in part (a) [Solution A] and 0.050 M NaOH (Solution B). Calculate the volume of Solution A that would yield the desired buffer when it is mixed with 250 mL of Solution B.

The predominant species in the buffer will be dihydrogen phosphate and monohydrogen phosphate. The relevant reaction is
$H_2PO_4^-(aq) + H_2O(l) \rightarrow HPO_4^{-2}(aq) + H_3O^+(aq)$ for which
$K_a = 10^{-7.21} = [H^+][HPO_4^{-2}]/[H_2PO_4^-]$. Substituting $[H^+] = 1.00 \times 10^{-7}$ M, one obtains the **ratio** $[HPO_4^{-2}]/[H_2PO_4^-] = 0.62$.

The 250 mL of solution B contains (0.250 mL)(0.05 M) = 0.013 moles of OH-. Sufficient solution A must be added to react completely with the base, producing 0.0125 mole of HPO_4^{-2}. However, an excess of solution A must be added so that at the end one has (0.013)/0.62 = 0.022 moles of $H_2PO_4^-$. One requires therefore sufficient solution A to provide 0.013 + 0.022 = 0.035 moles of $H_2PO_4^-$. This requires a volume of (0.035 mole)/(0.1 M) = 0.35 L.

4) (30 points) The solubility product of the mineral fluorite, CaF_2, is 1.46×10^{-10}. Calculate the solubility of fluorite in

a) pure water

The relevant reaction is $CaF_2(s) \rightarrow Ca^{+2}(aq) + 2 F^-(aq)$ so
$Ksp = 1.46 \times 10^{-10} = [Ca^{+2}][F^-]^2$. In part (a) the fluorite is the **sole** source of fluoride so from the stoichiometry of the reaction $2[Ca^{+2}] = [F^-]$. Substituting this result in the K_{sp} expression yields $1.46 \times 10^{-10} = 4[Ca^{+2}]^3$. One quickly obtains the solubility, $[Ca^{+2}] = 3.3 \times 10^{-4}$ M.

b) 0.20 M potassium fluoride

In part (b) the same Ksp expression applies but now the **dominant** source of fluoride is the fluoride present in the solution prior to adding the fluorite. Therefore, $1.46 \times 10^{-10} = [Ca^{+2}][0.20\ M]^2$. One quickly obtains the new solubility, $[Ca^{+2}] = 3.7 \times 10^{-9}$ M. By the common-ion effect, the solubility of fluorite has been suppressed.

5) (50 points) This problem deals with a 1 M solution of oxalic acid, a diprotic acid with the structural formula HOOC-COOH. [Relevant pK_a's can be found on the insert.]

a) In the space provided below, carefully sketch the concentration of HOOC-COOH (use a solid ——— line), $^-$OOC-COOH (use a dashed - - - - - - - - - line), and $^-$OOC-COO$^-$ (use a dotted ·········· line) as a function of pH.

To make the plot, one must recognize that the dominant species in the region between low pH and the first equivalence point are undissociated oxalic acid and monohydrogen oxalate. The dominant species between the first and second equivalence points are monohydrogen oxalate and oxalate. The dominant species above the second equivalence point is oxalate.

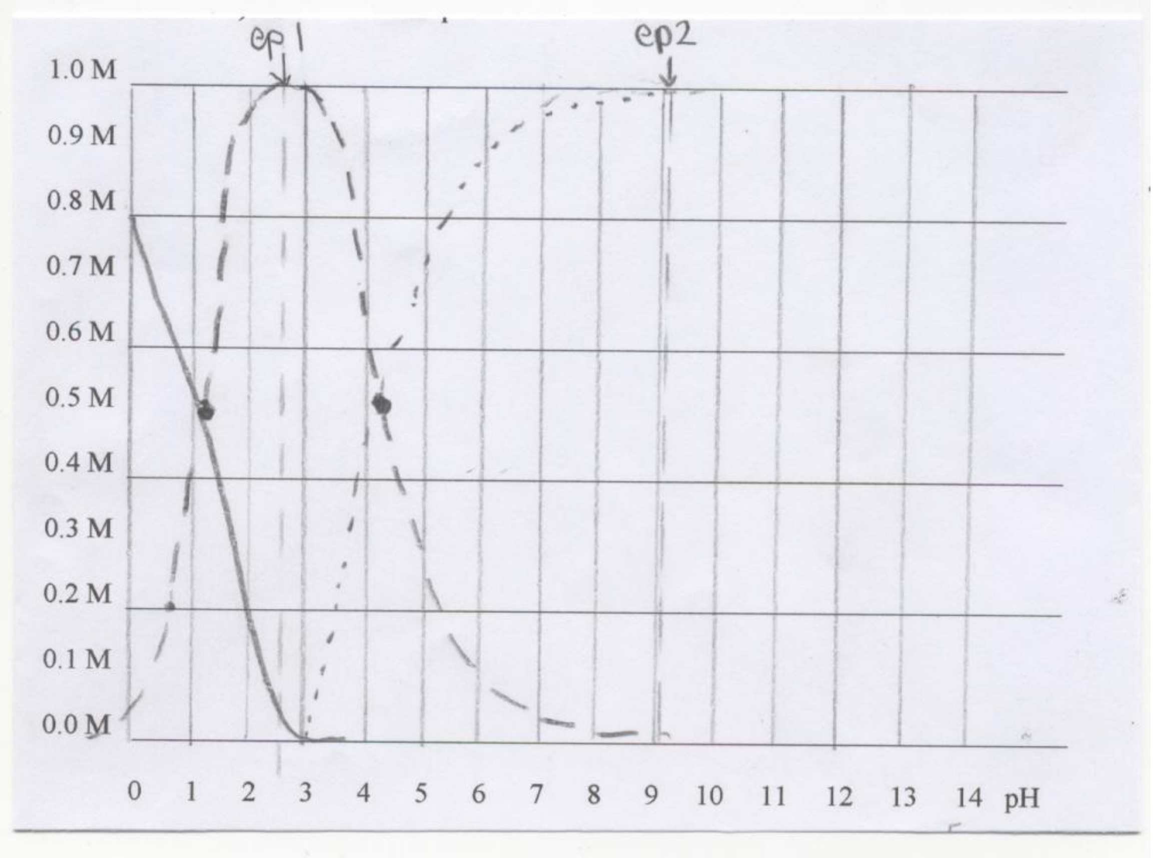
Construction of the plot is enabled by results are 6 points:
a) Pure oxalic acid in water. This is a pure acid problem. To a first iteration, [H+] = $(K_{a1}[H_2A]_0)^{0.5}$ or pH = 0.5pK_{a1} since $[H_2A]_0$ = 1 M. This yields pH 0.6, a number close to zero; a cycle of successive approximations yields a revised value for the pH, 0.7, and $[H^+]$ = [$^-$OOC-COOH] = 0.21 M and [HOOC-COOH] = 1.00 – 0.21 = 0.79 M.
b) The first halfway point is at pK_{a1} = 1.24 where [$^-$OOC-COOH] = [HOOC-COOH] = 0.5 M.
c) The first equivalence point where the dominant species is $^-$OOC-COOH is given by pH = 0.5(pK_{a1} + pK_{a2}) = 2.71.
d) The second halfway point is at pK_{a2} = 4.19 where [$^-$OOC-COO$^-$]= [HOOC-COO$^-$] = 0.5 M.
e) At the second equivalence point, oxalate is the dominant species. We have a pure base problem and the standard methods yield pH 9.10.

With these results one can construct the required plot. The concentration of oxalic acid is 0.79 M at pH 0.7, drops to 0.5 M at pH 1.23, and is very small at the first equivalence point. The concentration of monohydrogen oxalate is 0.21 M at pH 0.7, reaches 0.5 M at pH 1.23 and its maximum of nearly 1 M at the first equivalence point, drops to 0.5 M at pH 4.19, and is very small by the second equivalence point. The concentration of oxalate is very low until after the first equivalence point. It climbs to 0.5 M at pH 4.19 and nearly 1 M at the final equivalence point. Connecting these points in a manner with no wiggles and discontinuities yields the desired plots.

Note well. A distribution plot, not a titration curve was requested.

b) Estimate the concentrations of the two most abundant oxalate species at pH 5.0.

The pH lies between the second halfway point at pH 4.19 and the second equivalence point at pH 9.10. The dominant species are monohydrogen oxalate and oxalate. A calculation is not needed here. Simply read the points off the graph which can be sketched. One obtains [$^-$OOC-COO$^-$] ≈ 0.8 M and [HOOC-COO$^-$] ≈ 0.2 M.


ep1
ep2
1.0 M
0.9 M
0.8 M
0.7 M
0.6 M
0.5 M
0.4 M
0.3 M
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1
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3
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9
10
11
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13
14
pH

THIRD MIDTERM EXAMINATION
CHEMISTRY 1a, FALL, 2008
CORRECTED INSERT

TABLE OF pK_a's OF SELECTED ACIDS

Acid	Name of the Acid	pK_a
H_2O	water	14.00
HPO_4^{-2}	monohydrogen phosphate	12.32
$HTeO_4^-$	monohydrogen tellurate	11.00
HCO_3^-	monohydrogen carbonate	10.33
NH_4^+	ammonium	9.25
$HSeO_3^-$	monohydrogen selenite	8.32
$H_2PO_4^-$	dihydrogen phosphate	7.21
H_2TeO_3	tellurous acid	6.27
$C_2H_4O_2$	acetic acid	4.76
$C_2HO_4^-$	monohydrogen oxalate	4.19
$C_2H_4O_3$	glycolic acid	3.83
$C_2ClH_3O_2$	chloroacetic acid	2.69
HSO_4^-	monohydrogen sulfate	1.98
$C_2H_2O_4$	oxalic acid	1.23
HIO_3	iodic acid	0.78