24. $\mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{OH}^{-}$
A. Tots 0.160 m solon $\mathrm{CH}_{3} \mathrm{NH}_{3}$
4.700

$$
\begin{aligned}
& 0.160 \mathrm{M}(0.047): 7.5 \times 10^{-3} \mathrm{M} \quad\left[\mathrm{CH}_{3} N H_{2}\right]: 0.16-7.5 \times 10^{-3} \\
& 7.5 \times 10^{-3} \mathrm{M}=\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right]=[0 \mathrm{H}] \\
& =0.152 \\
& {\left[\mathrm{H}_{30^{+}}\right]=\frac{1.0 \times 10^{-14}}{7.5 \times 10^{-3}}=1.3 \times 10^{-12} \mathrm{M}} \\
& p H=11.89
\end{aligned}
$$

B. $3 p+s$

$$
\begin{aligned}
& K_{b}=\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right][\mathrm{OH}]}{\left[\mathrm{CH}_{3} \mathrm{NH} 2\right]} \\
& K_{b}=\frac{\left(7.5 \times 10^{-3}\right)^{2}}{0.152}=3.7 \times 10^{-4}
\end{aligned}
$$

C. $5 p+s$
0.050 mol $\mathrm{La}\left(\mathrm{NO}_{3}\right)_{3}$
$1.00<$ solution
$0.20 \operatorname{mog} \mathrm{CH}_{3} \mathrm{NH}_{2}$
$0.20 \mathrm{~mol} \mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$ wM La $(\mathrm{OH})_{3} \mathrm{pp+}$ ?

$$
\begin{aligned}
& K_{S P}=[L a+3][0+1]^{3}=1 \times 10^{-19} \\
& Q=\left[\frac{0.050}{1.00}\right]\left[3.7 \times 10^{-4}\right)^{3} \\
& Q=2.5 \times 10^{-12} \\
& Q>K_{S \rho}
\end{aligned}
$$

yes, $\mathrm{La}(\mathrm{OH})_{3}$ pets
25.
a) two points
${ }^{1}$ S increases
Dissolving converts highly organized solid to less organized hydrated ions
OR
dissociates, break down, etc.
OR
less particles => more particles
OR
${ }^{1} \mathrm{G}$ negative, ${ }^{1} \mathrm{H}$ positive $=>-\mathrm{T}^{1} \mathrm{~S}$ negative $=>{ }^{1} \mathrm{~S}$ positive
b) two points

Ksp decreases
lowering T decreases the solubility since the reaction is endothermic
OR
if T decreases, $-\mathrm{T}^{1} \mathrm{~S}$ becomes less negative or ${ }^{1} \mathrm{G}$ becomes
more positive, i.e., less soluble; Ksp decreases
c) two points

There is no effect on [l]
PbI 2 is a solid; its concentration does NOT change on addition of more Pbl2
OR
$\mathrm{PbI} 2(\mathrm{~s})$ is NOT included in the expression for Ksp or Q OR
the solution is saturated => no more solid will dissolve
d) two points
${ }^{1} \mathrm{G}$ becomes more positive (increases, gets larger, etc.)
Due to the common ion effect; the increase in [Pb2+] shifts the equilibrium to the left.
OR
the reverse reaction becomes more spontaneous as [Pb2+] increases due to the common ion effect
a)
$5.00 \times 10^{-3} \mathrm{~mol} \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}=1.00 \times 10^{-2} \mathrm{~mol} \mathrm{H}^{+}=1.00 \times 10^{-2} \mathrm{~mol} \mathrm{OH}^{-}$ $1.00 \times 10^{-2} \mathrm{~mol} \mathrm{OH}^{-} / 0.400 \mathrm{M}=0.0250 \mathrm{~L}(25.0 \mathrm{~mL})$.
Calculation from moles to volume; use of incorrect moles still earns point.

## b)

There are two successive dissociations:
$\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ <===> $\mathrm{H}^{+}+\mathrm{HC}_{2} \mathrm{O}_{4}{ }^{-}$(equilibrium constant $=\mathrm{K}_{1}$ ) $\mathrm{HC}_{2} \mathrm{O}_{4}{ }^{-}<===>\mathrm{H}^{+}+\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$ (equilibrium constant $=\mathrm{K}_{2}$ )
Acceptable alternatives are the use of $\mathrm{H}_{2} \mathrm{O}$ as reactant and $\mathrm{H}_{3} \mathrm{O}^{+}$as product or writing of correct equilibrium constant expressions. Consistent errors (such as missing atoms or charges) are only penalized once.
c)
$\mathrm{pH}=0.5$ therefore $\mathrm{H}^{+}=0.32 \mathrm{M}$ ( pH controls 1 sig. fig. in answer) (This point also earned if conversion of K to pK is correct.)
K small therefore amount of dissociation small therefore assume $\left[\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}\right]=0.015$
$\mathrm{K}_{12}=\left(\left[\mathrm{H}^{+}\right]^{2}\left[\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}\right]\right) /\left[\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}\right]$,
then $\left[\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}\right]=\left[\left(3.78 \times 10^{-6}\right)(0.015)\right] /(0.32)^{2}=6 \times 10^{-7}$.
(Here 1, 2 , or 3 sig. fig.'s accepted) Two points for correct set-up with substitution and final calculation (-1 point for each error).
Alternative methods, included proper use of Henderson-Hasselbalch equation, can earn credit.
(d)
$\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}+\mathrm{H}_{2} \mathrm{O}<===>\mathrm{HC}_{2} \mathrm{O}_{4}^{-}+\mathrm{OH}^{-}$is the only significant reaction, so $\mathrm{Kb}=\mathrm{Kw} / \mathrm{K} 2=1.00 \times 10^{-14} / 6.40 \times 10^{-5}=1.56 \times 10^{-10}$
No credit earned if $\mathrm{K}_{1}$ or $\mathrm{K}_{12}$ used; 1 , 2 , or 3 sig. fig.'s accepted since number of significant figures for value of Kw not indicated in table on examination.

$$
\begin{aligned}
& \text { 20. } \mathrm{CH}_{3} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}^{+}+\mathrm{H}^{-} \\
& \text {A. } 3 \rho+5 K_{b}=\frac{\left[\mathrm{CH}_{3} \sim_{3}^{+}\right]\left[\mathrm{CH}^{-}\right]}{\left[\mathrm{cH}_{3} \mathrm{NH}_{2}\right]}=5.24 \times 10^{-4} \\
& \begin{array}{cccc} 
& {\left[\mathrm{CH}_{3} \sim_{2}\right]} & {\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right]} & {\left[0 \mathrm{H}^{-}\right.} \\
1 & 0.225 & 0 & 0 \\
C & -x & +x & +x \\
\leftarrow & 0.225-1 & x & x
\end{array} \\
& 5.25 \times 10^{-4}=\frac{x^{2}}{0.225} \\
& x=\left[\mathrm{OH}^{-}\right]=1.09 \times 10^{-2} \\
& \text { B. } 3+5 \\
& \mathrm{NO}_{3}^{-} \text {) }
\end{aligned}
$$

$0.0100 \mathrm{~mol}\left(\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right)($
$120.0 \mathrm{~ms} 0.225 \mathrm{M} \mathrm{CH}_{3} \mathrm{NH}_{2}$

$$
\begin{gathered}
{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right]=\frac{0.0100 \mathrm{wol}}{0.120 \mathrm{~L}}=0.0833 \mathrm{M}} \\
5.25 \times 10^{-4}=\frac{(0.0833)(x)}{(0.225)} \\
x=[0 H-]=1.42 \times 10^{-3} \mathrm{M} \\
\text { oOH }=2.85 \quad \quad \mathrm{PH}=11.15
\end{gathered}
$$

$05 \mathrm{pH}=\mathrm{pka}^{k}+\log \frac{b a f e}{a c i d}$

$$
p H=10.7+\frac{0.225}{0.0833}
$$

C. ? pts
want $\rho H=11$ (NOUH or $H(1)$ HEl added

$$
\begin{aligned}
& \rho H=\rho K a+\log \frac{b u s e}{a c i} d \\
& 11.00=10.72+\log \frac{b a f e}{a \operatorname{acd}} \\
& L_{\mathrm{j}}=0.28 \quad \frac{\text { base }}{\text { acid }}=1.406=\frac{\left[\mathrm{CH}_{3} N H_{3}^{+}-x\right]}{\left[\mathrm{CH}_{3} N H_{2}+x\right]} \\
& x=0.0227 \mu \\
& (0.0227 \mathrm{M})(0.120 \mathrm{~L})=2.73 \times 10^{-3} \mathrm{~mol} \mathrm{HCl}
\end{aligned}
$$

D.

The $\frac{\left[\mathrm{CH}_{3} \sim_{3}^{+}\right]}{\left[\mathrm{CH}_{3} \sim \mathrm{H}_{2}\right]}$ ratio does not change $m$ the buffer solution
21. $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \longrightarrow 2 \mathrm{H}^{+}+\mathrm{C}_{2} \mathrm{O}_{4}^{-2} \quad \mathrm{~K}=3.78 \times{ }^{-6}$
A. $0.400 \mathrm{M} \mathrm{NaOH} \quad 5.00 \times 10^{-3}$ mol HA
S.00 $\times 10^{-3}$ mole HA produces $1.00 \times 10^{-2} \mathrm{molh} \mathrm{H}^{+}$
(diprotic)
$1.00 \times 10^{-2}$ mole $\mathrm{H}^{+}$needs $1.00 \times 10^{-2}$ mulo ot4-

$$
\frac{1.00 \times 10^{-2} \mathrm{moloH}}{}-100 \mathrm{M} \quad=0.0250 \mathrm{~L}(25.0 \mathrm{ml})
$$

B.

$$
\begin{aligned}
& \mathrm{K}_{2}=6.40 \times 10^{-5} \\
& \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \rightleftharpoons \mathrm{H}^{+}+\mathrm{HC}_{2} \mathrm{O}_{4}^{-} K_{1} \\
& \mathrm{HC}_{2} \mathrm{O}_{4}^{-} \rightleftharpoons \mathrm{H}_{2} \mathrm{O}_{4}^{-2} K_{2} \\
& K=K_{1} \times \mathrm{K}_{2}
\end{aligned}
$$

$$
\begin{aligned}
& \text { D. } \mathrm{C}_{2} \mathrm{O}_{4}^{-2}+\mathrm{H}_{2} \mathrm{~F} \rightleftharpoons H \mathrm{C}_{2} \mathrm{O}_{4}^{-}+0 \mathrm{H}- \\
& K_{b}=\frac{K_{\omega}}{K_{2}}=\frac{1.00 \times 10^{-14}}{6.40 \times 10^{-5}}=1.56 \times 10^{-10}
\end{aligned}
$$

