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## Chemistry 2000 Practice Final A

## INSTRUCTIONS

1) Read the exam carefully before beginning. There are 15 questions on pages 2 to 14 followed by 2 pages of data/formulas/periodic table as well as a blank page for rough work. Please ensure that you have a complete exam. If not, let an invigilator know immediately. All pages must be submitted at the end of the exam.
2) If your work is not legible, it will be given a mark of zero.
3) Marks will be deducted for incorrect information added to an otherwise correct answer.
4) Marks will be deducted for improper use of significant figures and/or missing units.
5) Show your work for all calculations. Numerical answers without supporting calculations will not be given full credit.
6) You may use a calculator but only for calculation. No text-capable calculators are allowed.
7) DO NOT OPEN THE EXAM UNTIL YOU ARE TOLD TO BEGIN. Beginning prematurely will result in removal of your exam paper and a mark of $\mathbf{0}$.
8) You have $\mathbf{3}$ hours to complete this exam. Nobody may leave the exam room during the first hour or the last 15 minutes of the exam.

| $Q$ | Mark |
| :---: | :---: |
| 1 | $/ 14$ |
| 2 | $/ 3$ |
| 3 | $/ 6$ |
| 4 | $/ 6$ |
| 5 | $/ 7$ |
| 6 | $/ 13$ |
| 7 | $/ 6$ |
| 8 |  |


| $Q$ | Mark |
| :---: | :---: |
| 9 | $/ 8$ |
| 10 | $/ 3$ |
| 11 | $/ 5$ |
| 12 | $/ 6$ |
| 13 | $/ 1$ |
| 14 |  |
| 15 |  |
|  |  |


| Total | $/ 110$ |
| :--- | :--- |

$\qquad$

1. Fill in each blank with the word or short phrase that best completes the sentence.
[14 marks]
(a) Conduction of electricity is possible when the energy required to excite an electron from the _valence_ band into the _conduction_ band is small.
(b) A(n) _n_-type semiconductor has been doped to contain extra electrons.
(c) Vibrational energy spacings correspond to the _infrared or $\mathbb{I R}$ _ region of the electromagnetic spectrum.
(d) According to valence bond theory, the nitrogen atom in $\mathrm{NH}_{3}$ is $\mathrm{Sp}^{3} \_$hybridized.
(e) The conjugate acid of $\mathrm{NH}_{3}$ is $\mathrm{NH}_{4}^{+}$.
(f) The conjugate base of $\mathrm{NH}_{3}$ is $\mathrm{NH}_{2}^{-}$.
(g) When $\Delta_{r} G^{\circ}>0$, the reaction is _favoured in the reverse direction under standard conditions or not favoured under standard conditions_.

Technically, the first answer given is better since, if $\Delta_{r} G^{\circ}=0$, the reaction is not favoured in either direction under standard conditions. You may prefer to say "thermodynamically allowed" instead of "favoured".

The "under standard conditions" part is important. Many reactions that are reactant-favoured under standard conditions can be made to be product favoured by changing temperature and/or the amount of products and reactants. "Under standard conditions" means that all products and reactants have activities of 1 - so they are either solids, pure liquids, ideal solutes at $1 \mathrm{~mol} / \mathrm{L}$, or gases at 1 bar.
(h) In the equation $S=k_{B} \ln \Omega, S$ represents _entropy_ and $\Omega$ represents _number of microstates_.
(i) A substance which has the density of a liquid but whose particles have high enough energy that they do not feel intermolecular forces is a _supercritical fluid_.
(j) The temperature and pressure at which a substance is in equilibrium between the solid, liquid and gas phases is known as the _triple point_.
(k) Raoult's law demonstrates that dissolving a non-volatile solute in a liquid _decreases_ the vapour pressure above that liquid.
(l) Two molecules that are nonsuperimposable mirror images are best described as a pair of _enantiomers_.
$\qquad$
2. Consider the following three molecules.

(a) Circle any of these molecules which are chiral.
(b) Mark all chirality centers on all the molecules above with a *.
3. Circle and label the functional groups in heroin (shown below): It must be clear which functional group name goes with each circle.

4. The chemical structure of isoprene is shown at the left below. When isoprene is reacted with HBr , a carbocation is formed, as shown, in the first step of a two-step reaction.

(a) Add curly arrows to the diagram above to show how the carbocation is formed. [2 marks]
(b) Add curly arrows to the diagram above to show what happens in the second step. [1 mark]
(c) On the diagram above, draw the product(s) of the second step. [1 mark]
(d) In theory, four different carbocations could have been produced by reacting isoprene with HBr . Briefly, explain why the one shown is the best. There are two important factors to address. You may find it helpful to include a diagram in your answer.

1. The carbocation shown is a $3^{\circ}$ carbocation (meaning that there are three carbon atoms attached to the carbon atom with the positive charge). None of the other three carbocations that could be formed are $3^{\circ}$. Carbocations that are more highly substituted tend to be more stable.
2. The carbocation shown is resonance-stabilized. A second resonance structure can be drawn in which the positive charge is on a different carbon atom. Thus, the positive charge is delocalized (shared by the two carbon atoms) so that neither carbon atom has to bear the full +1 charge. Instead, each carbon atom has a fractional positive charge (in the true structure - which is a weighted average of the two resonance structures).

3. 

(a) Draw all isomers of $\mathrm{C}_{3} \mathrm{H}_{5} \mathrm{Cl}$.

You may either draw expanded structures or use line-bond notation.
Marks will be deducted for incorrect or duplicate answers.





(b) Consider the set of molecules you just drew as your answer to part (a).

In the space below, redraw any pairs of stereoisomers and clearly indicate what makes them stereoisomers.
[2 marks]

trans isomer

cis isomer
$\qquad$
6. Boron monofluoride (BF) is an unstable gas in isolation but has been found to exist as a stable ligand when combined with transition metals.
[13 marks]
(a) Draw a Lewis diagram for boron monofluoride. Include any nonzero formal charges.
This is a terrible horrible Lewis diagram, but it's the only way to make both B and F obey the octet rule. Basically, as awful as this is, there isn't a better Lewis diagram. To make both atoms neutral, you would need a single bond with one lone pair on B and three lone pairs on F. Admittedly, looking at pictures of the MOs suggests that that diagram may be closer to reality than the one above.
(b) What bond order does your Lewis diagram predict?
[1 mark]
3
(c) Draw a valence molecular orbital energy level diagram for BF.
[9 marks]

- Label all of the atomic and molecular orbitals. To the best of your ability, clearly indicate whether each molecular orbital is bonding, nonbonding or antibonding.
- Include the lines to show the linear combinations that form each MO.
- Populate the atomic orbitals and the molecular orbitals with electrons.

You do NOT have to draw pictures of the orbitals on your diagram. Just show the energy levels and which atomic orbitals combine to make each molecular orbital.


## Key Points:

- $1 \mathrm{~s}(\mathrm{~B})$ and $1 \mathrm{~s}(\mathrm{~F})$ are core AOs. They do not contribute to the valence MOs.
- $2 s(F)$ is more than 1 Ry away from the nearest AO (2s(B) is 1.58 Ry higher in energy), so $2 \mathrm{~s}(\mathrm{~F})$ has nothing to combine with and turns into a sigma symmetric nonbonding MO: $1 \sigma_{\mathrm{nb}}$.
- $2 p_{x}(B)$ and $2 p_{x}(F)$ combine to give two pi symmetric MOs: $1 \pi$ and $2 \pi^{*}$. The energy gap between $2 p(B)$ and $2 \mathrm{p}(\mathrm{F})$ is almost 1 Ry , so $1 \pi$ is mostly on F and $2 \pi^{*}$ is mostly on B.
- $2 \mathrm{pyy}_{\mathrm{y}}(\mathrm{B})$ and $2 \mathrm{pyy}_{\mathrm{y}}(\mathrm{F})$ combine to give two pi symmetric MOs: $1 \pi$ and $2 \pi^{*}$ (perpendicular to the ones from the $2 p_{x}$ AOs, but otherwise identical to them)
- $2 \mathrm{~s}(\mathrm{~B}), 2 \mathrm{p}_{\mathrm{z}}(\mathrm{B})$ and $2 \mathrm{p}_{\mathrm{z}}(\mathrm{F})$ combine to give three sigma symmetric MOs: $2 \sigma, 3 \sigma_{n b}$ and $4 \sigma^{*}$.
o $2 \sigma$ must be lower in energy than all three AOs
o $4 \sigma^{*}$ must be higher in energy than all three AOs
o $3 \sigma_{\mathrm{nb}}$ should have an energy somewhere between $2 \sigma$ and $4 \sigma^{*}$
(d) Write the valence orbital occupancy (i.e., electron configuration) in line notation for BF. [1 mark] $\left(1 \sigma_{n b}\right)^{2}(2 \sigma)^{2}(1 \pi)^{4}\left(3 \sigma_{n b}\right)^{2}$
(e) What bond order does your molecular orbital diagram predict for BF?

$$
\begin{array}{ll}
\frac{(6-0)}{2}=3 & 6 \text { bonding electrons; } 0 \text { antibonding electrons; } 4 \text { nonbonding electrons; } \\
& \text { nonbonding electrons don't affect bond order }
\end{array}
$$

$\qquad$
7. The figure below shows a molecular orbital energy level diagram for ethyne (formerly known as acetylene). The energy levels for the atomic orbitals of each half of the molecule (one carbon atom and one hydrogen atom) are shown on the left and right. Lines connecting the atomic orbitals of the hydrogen atoms to the corresponding molecular orbitals have been omitted for clarity. There is a line (not shown) from each $H(1 s)$ to every sigma MO.
[15 marks]

(a) Complete the diagram above by adding electrons to the molecular orbitals.
(b) Which orbital is the HOMO?
(c) Which orbital is the LUMO?
(d) If ethyne were to act as a nucleophile in a reaction, which orbital(s) would it use? [1 mark] $1 \pi$
$\qquad$
7. continued...
(e) In the space below, sketch the three sigma bonding molecular orbitals for ethyne. You may sketch the molecular orbital or sketch the superposition of the atomic orbitals. Clearly label each sketch so that we know which molecular orbital it shows.
[3 marks]

$2 \sigma$


3б

from:

(f) The pictures below show the calculated $\sigma^{*}$ orbitals for ethyne.
[3 marks] Underneath each picture, label the orbital as $4 \sigma^{*}, 5 \sigma^{*}$ or $6 \sigma^{*}$.

(g) If ethyne were considered according to valence bond model, what would be the hybridization of the C atoms?
[1 mark]
$s p$
(h) In comparing the the MO and VB models of the bonding in ethyne, what is the same? [2 marks]

The bond orders are the same according to both models. Both models give C-H bond orders of 1 and a $\mathrm{C} \equiv \mathrm{C}$ bond order of 3 .

According to both models, the $\mathrm{C} \equiv \mathrm{C}$ triple bond consists of one $\sigma$ bond and two $\pi$ bonds.
(i) In comparing the the MO and VB models of the bonding in ethyne, what is different?

The VB model treats all bonds as though they were localized. As such, it suggests three distinct $\sigma$ bonds - one between the two carbon atoms, and two localized C-H $\sigma$ bonds.

The MO model suggests that the electrons in the three $\sigma$ bonding MOs are delocalized (shared) across all four atoms in the molecule. This is shown in the answers to part (e).

Name:
8. A common demonstration is to generate carbon dioxide in a test tube by heating a sample of solid magnesium carbonate:

$$
\mathrm{MgCO}_{3(s)} \rightarrow \mathrm{MgO}_{(s)}+\mathrm{CO}_{2(g)}
$$

(a) Is $\Delta_{\mathrm{r}} \mathrm{G}$ positive, negative or zero for this reaction? Briefly, justify your answer.

Negative.

The reaction proceeds therefore it must be thermodynamically allowed under these conditions. $\Delta_{r} G<0$ for all reactions that are thermodynamically allowed.
(b) Is $\Delta_{\mathrm{r}} \mathrm{S}$ positive, negative or zero for this reaction? Briefly, justify your answer.
[2 marks]

Positive.

The reaction generates a gas (and consumes no gases). When a reaction produces more moles of gas than it consumes, the entropy of the system increases because gases have high entropy (large numbers of possible microstates).
(c) Is $\Delta_{\mathrm{r}} \mathrm{H}$ positive, negative or zero for this reaction? Briefly, justify your answer.

It is likely to be positive.*

The fact that the reaction must be heated suggests that it is likely endothermic. Endothermic reactions have positive values for enthalpy change.
*As some students pointed out, we cannot know for certain that this reaction is endothermic. If the reaction were exothermic (negative $\Delta_{r} H$ ), it would still be product-favoured at high temperatures. It is possible that the heating is required to overcome the activation energy of the reaction - but not actually required to make the reaction product-favoured. Explanations of this nature were given full credit.
9. Consider the equilibrium expression below:
[8 marks]

$$
P C l_{5}(g) \rightleftharpoons P C l_{3}(g)+C l_{2}(g)
$$

Is this reaction favoured in the forward or reverse direction if the partial pressures of the initial mixture are 0.123 bar $\left(P C l_{5}\right), 0.456$ bar $\left(P C l_{3}\right)$, and 0.789 bar $\left(C l_{2}\right)$ and the temperature is $25.00^{\circ} \mathrm{C}$ ?

There are two approaches to this question. Both require calculation of $\Delta_{r} G^{\circ}$ and $Q$. Both also require converting the temperature into Kelvin.
A. Calculate $\Delta_{r} G$ from $\Delta_{r} G^{\circ}$ using $\Delta_{r} G=\Delta_{r} G^{\circ}+R T \ln Q$

- If $\Delta_{r} G$ is negative, the reaction is favoured in the forward direction.
- If $\Delta_{r} G$ is positive, the reaction is favoured in the reverse direction.
B. Calculate $K$ from $\Delta_{r} G^{\circ}$ using $\Delta_{r} G^{\circ}=-R T \ln K$
- If $Q<K$, the reaction is favoured in the forward direction.
- If $Q>K$, the reaction is favoured in the reverse direction.

Step 1: Calculate the reaction quotient $(Q)$ from the activities

$$
Q=\frac{a_{P C l_{3}(g)} \cdot a_{C l_{2}(g)}}{a_{P C l_{5}(g)}}=\frac{\left(\frac{0.456 \mathrm{bar}}{1 \text { bar }}\right)\left(\frac{0.789 \mathrm{bar}}{1 \mathrm{bar}}\right)}{\left(\frac{0.123 \mathrm{bar}}{1 \text { bar }}\right)}=\frac{(0.456)(0.789)}{(0.123)}=2.93
$$

Step 2: Calculate $\Delta_{r} G^{\circ}$ from $\Delta_{f} G^{\circ}$ values on the data sheet

$$
\begin{aligned}
& \Delta_{r} G^{\circ}=\sum \Delta_{f} G^{\circ}(\text { products })-\sum \Delta_{f} G^{\circ}(\text { reactants }) \\
& \Delta_{r} G^{\circ}=\Delta_{f} G^{\circ}\left(P C l_{3}(g)\right)+\Delta_{f} G^{\circ}\left(C l_{2}(g)\right)-\Delta_{f} G^{\circ}\left(\text { PCl }_{5}(g)\right) \\
& \Delta_{r} G^{\circ}=\left(-268 \frac{k J}{\mathrm{~mol}}\right)+\left(0 \frac{\mathrm{~kJ}}{\mathrm{~mol}}\right)-\left(-323 \frac{\mathrm{~kJ}}{\mathrm{~mol}}\right) \\
& \Delta_{r} G^{\circ}=55 \frac{\mathrm{~kJ}}{\mathrm{~mol}}
\end{aligned}
$$

Step 3: Convert temperature into Kelvin

$$
T=25.00+273.15=298.15 \mathrm{~K}
$$

Step 4A: Calculate $\Delta_{r} G$ from $\Delta_{r} G^{\circ}$ using $\Delta_{r} G=\Delta_{r} G^{\circ}+R T \ln Q$

$$
\begin{aligned}
& \Delta_{r} G=\Delta_{r} G^{\circ}+R T \ln Q \\
& \Delta_{r} G=\left(55 \frac{\mathrm{~kJ}}{\mathrm{~mol}}\right)+\left(8.314462 \frac{\mathrm{~J}}{\mathrm{~mol} \cdot \mathrm{~K}}\right)\left(\frac{1 \mathrm{~kJ}}{1000 \mathrm{~J}}\right)(298.15 \mathrm{~K}) \ln (2.93) \\
& \Delta_{r} G=\left(55 \frac{\mathrm{~kJ}}{\mathrm{~mol}}\right)+\left(2.66 \frac{\mathrm{~kJ}}{\mathrm{~mol}}\right) \\
& \Delta_{r} G=58 \frac{\mathrm{~kJ}}{\mathrm{~mol}} \quad 0 \text { decimal places therefore } 2 \text { sig. fig. }
\end{aligned}
$$

Therefore $\Delta_{r} G>0$ therefore the reaction is favoured in the reverse direction under these conditions.
Step 4B: Calculate $K$ from $\Delta_{r} G^{\circ}$ using $\Delta_{r} G^{\circ}=-R T \ln K$

$$
\Delta_{r} G^{\circ}=-R T \ln K \quad \text { therefore } \quad \ln K=-\frac{\Delta_{r} G^{\circ}}{R T} \quad \text { therefore } \quad K=e^{-\frac{\Delta_{r} G^{\circ}}{R T}}
$$

$$
K=e^{-\frac{\left(55 \frac{\mathrm{~kJ}}{\mathrm{~mol})\left(\frac{1000 J}{1 \mathrm{~kJ}}\right)}\right.}{\left(8.314462 \frac{J}{\mathrm{~mol} \cdot \mathrm{~K}}\right)((298.15 \mathrm{~K}))}}=e^{-22}=2 \times 10^{-10}
$$

0 decimal places in the exponent means 0 sig. fig. (only the " $\times 10^{-10 \text { " }}$ part is significant) - but that's hard to write, so I've written 1 sig. fig. here.
Therefore $Q>K$ therefore the reaction is favoured in the reverse direction under these conditions.
10. Briefly demonstrate how the formula $\Delta_{r} G^{\circ}=-R T \ln K$ is derived from $\Delta_{r} G=\Delta_{r} G^{\circ}+R T \ln Q$. Your logic must be clear (which may require you to define terms).
At equilibrium, $\Delta_{r} G=0$ since the reaction is neither favoured in the forward nor reverse direction.
At equilibrium, $Q=K$.
Making those two substitutions into $\Delta_{r} G=\Delta_{r} G^{\circ}+R T \ln Q$ gives

$$
0=\Delta_{r} G^{\circ}+R T \ln K
$$

Therefore:

$$
-R T \ln K=\Delta_{r} G^{\circ} \quad \text { or } \quad \Delta_{r} G^{\circ}=-R T \ln K
$$

11. Zinc metal can be used to convert $\mathrm{VO}_{2}{ }^{+}$into $\mathrm{VO}^{2+}$ in aqueous acid.

An incomplete and unbalanced equation for this process is shown below:

$$
V O_{2}^{+}(a q)+Z n(s) \rightarrow V O^{2+}(a q)+Z n^{2+}(a q)
$$

(a) What is the oxidation state of V in $\mathrm{VO}_{2}{ }^{+}$?
$+5$
(b) What is the oxidation state of V in $\mathrm{VO}^{2+}$ ?
$+4$
(c) Is Zn acting as an oxidizing agent or a reducing agent in this reaction? How do you know?

Reducing agent. Its loss of electrons allows V to be reduced from +5 to +4 .
(d) Write a balanced chemical equation for this process.

$$
2 \mathrm{VO}_{2}^{+}(a q)+\mathrm{Zn}(s)+4 \mathrm{H}^{+}(a q) \rightarrow 2 \mathrm{VO}^{2+}(a q)+\mathrm{Zn}^{2+}(a q)+2 \mathrm{H}_{2} \mathrm{O}(l)
$$

$\qquad$
(a) These cells always have the same value of $\mathrm{E}^{\circ}$. What is the value for $\mathrm{E}^{\circ}$ for all concentration cells? $E^{\circ}=0 \mathrm{~V}$
[1 mark]
(b) Using the $\mathrm{Cu} / \mathrm{Cu}^{2+}$ concentration cell as an example, write an equation for the half-reaction that takes place at the anode.

$$
C u_{(s)} \rightarrow \mathrm{Cu}_{(a q)}^{2+}+2 e^{-}
$$

(c) Using the $\mathrm{Cu} / \mathrm{Cu}^{2+}$ concentration cell as an example, write an equation for the half-reaction that takes place at the cathode.

$$
C u_{(a q)}^{2+}+2 e^{-} \rightarrow C u_{(s)}
$$

(d) Consider the following list of possible concentration cells.
[1 mark]
Circle all of the examples listed that would have a positive cell potential, E.

| $\substack{\text { i. }}$ | $C u_{(s)}\left\|C u_{(a q)}^{2+}(0.020 M) \\| C u_{(a q)}^{2+}(0.060 M)\right\| C u_{(s)}$ |
| :---: | :--- |
| ii. | $C u_{(s)}\left\|C u_{(a q)}^{2+}(0.040 M) \\| C u_{(a q)}^{2+}(0.060 M)\right\| C u_{(s)}$ |
| iii. | $C u_{(s)}\left\|C u_{(a q)}^{2+}(0.060 M) \\| C u_{(a q)}^{2+}(0.060 M)\right\| C u_{(s)}$ |
| iv. | $C u_{(s)}\left\|C u_{(a q)}^{2+}(0.080 M) \\| C u_{(a q)}^{2+}(0.060 M)\right\| C u_{(s)}$ |
| v. | $C u_{(s)}\left\|C u_{(a q)}^{2+}(0.100 M) \\| C u_{(a q)}^{2+}(0.060 M)\right\| C u_{(s)}$ |

A positive cell potential corresponds to a process that is favoured in the forward direction (i.e. with the half-reactions shown in parts (b) and (c)).

You would expect the process to be favoured in the forward direction if the process would even out the two concentrations of $\mathrm{Cu}^{2+}$ cations. That means that the concentration of $\mathrm{Cu}^{2+}$ cations should be higher at the cathode than at the anode (since the cathode is where $\mathrm{Cu}^{2+}$ is reduced to Cu while the anode is where Cu is oxidized to $\mathrm{Cu}^{2+}$ ).
The convention for cell notation is that the cathode is on the right and the anode is on the left. Therefore, you want the concentration on the right to be higher than the concentration on the left.
(e) For one of the answers you circled in part (d), calculate E at $25.00^{\circ} \mathrm{C}$.

The following is a fully worked solution for option $i$. The alternative numbers that would be obtained for the other options are shown at the end.
This is a Nernst equation calculation: $E=E^{\circ}-\frac{R T}{v_{e} F} \ln Q$.
Step 1: Find $E^{\circ}$
In part (a), we established that $E^{\circ}=0 \mathrm{~V}$
Step 2: Find $v_{\mathrm{e}}$
Adding the half-reactions in parts (b) and (c) gives:
$C u_{(s)}($ anode $)+C u_{(a q)}^{2+}($ cathode $)+2 e^{-} \rightarrow C u_{(s)}($ cathode $)+C u_{(a q)}^{2+}($ anode $)+2 e^{-}$
Because there are 2 electrons to cancel out, $v_{e}=2$.

Step 3: Convert temperature into Kelvin

$$
T=25.00+273.15=298.15 \mathrm{~K}
$$

Step 4: Calculate $Q$ from activities.

$$
Q=\frac{a_{\text {products }}}{a_{\text {reactants }}}=\frac{a_{C u(s)-\text { cathode }} \cdot a_{C u^{2}+(\text { aq })-\text { anode }}}{a_{C u(s)-\text { anode }} \cdot a_{C u^{2+(a q)}-\text { cathode }}}=\frac{(1)\left(\frac{0.020 M}{1 M}\right)}{(1)\left(\frac{0.06 M}{1 M}\right)}=\frac{0.020}{0.060}=\frac{1}{3}=0.33
$$

Step 5: Calculate $E$ using the Nernst equation. (R and F are constants.)

$$
E=(0 \mathrm{~V})-\frac{\left(8.314462 \frac{J}{\mathrm{~mol} \cdot \mathrm{~K}}\right)(298.15 \mathrm{~K})\left(\frac{1 \mathrm{~V}}{1 \mathrm{~J} / \mathrm{C}}\right)}{(2)\left(96485 \frac{\mathrm{C}}{\mathrm{~mol}}\right)} \ln (0.33)
$$

taking a logarithm of a number with 2 sig. fig. gives an answer with 2 decimal places (in this case, that's 3 sig. fig.)
$E=(0 \mathrm{~V})-(0.012846 \mathrm{~V})(-1.10)$
$E=(0 \mathrm{~V})-(-0.0141 \mathrm{~V})$
$E=+0.0141 \mathrm{~V}$
3 sig. fig.
Step 6: Check your work.
You were supposed to get an answer that was positive. This answer is positive.
Option ii:
$Q=\frac{a_{\text {products }}}{a_{\text {reactants }}}=\frac{a_{C u(s)-\text { cathode }} \cdot a_{\left.C u^{2+( } \text { aq }\right)- \text { anode }}}{a_{C u(s)-\text { anode }} \cdot a_{C u^{2+(a q)-c a t h o d e ~}}}=\frac{(1)\left(\frac{0.040 M}{1 M}\right)}{(1)\left(\frac{0.060}{1 M}\right)}=\frac{0.040}{0.060}=\frac{2}{3}=0.67$ 2 sig. fig.
$E=+0.0052 \mathrm{~V}$
2 sig. fig.
Answer is positive. We are happy.
Option iii:
$Q=\frac{a_{\text {products }}}{a_{\text {reactants }}}=\frac{a_{C u(s)-\text { cathode }} \cdot a_{C u^{2+}(\text { aq })-\text { anode }}}{a_{C u(s)-\text { anode }} \cdot a_{C u}{ }^{2+(\text { aq })-\text { cathode }}}=\frac{(1)\left(\frac{0.060 M}{1 M}\right)}{(1)\left(\frac{0.060 M}{1 M}\right)}=\frac{0.060}{0.060}=1.0$ 2 sig. fig.
$E=0 \mathrm{~V}$
Answer is not positive. We are not happy.
Time to double check work and, if we find no errors, re-evaluate answer to part (d)!
Option iv:
$Q=\frac{a_{\text {products }}}{a_{\text {reactants }}}=\frac{a_{C u(s)-\text { cathode }} \cdot a_{C u^{2+}}{ }_{\text {aqq }} \text {-anode }}{} a_{C u(s)-\text { anode }} \cdot a_{C u^{2}+(\text { aq })-\text { cathode }} \quad \frac{(1)\left(\frac{0.080 M}{1 M}\right)}{(1)\left(\frac{0.060 M}{1 M}\right)}=\frac{0.080}{0.060}=\frac{4}{3}=1.3$
2 sig. fig.
$E=-0.0037 \mathrm{~V}$ 2 sig. fig.
Answer is not positive. We are not happy.
Time to double check work and, if we find no errors, re-evaluate answer to part (d)!
Option v:
$Q=\frac{a_{\text {products }}}{a_{\text {reactants }}}=\frac{a_{C u(s)-\text { cathode }} \cdot a_{C u^{2+}(\text { aq })-\text { anode }}}{a_{C u(s)-\text { anode }} \cdot a_{C u^{2}+(a q)-\text { cathode }}}=\frac{(1)\left(\frac{0.100 M}{1 M}\right)}{(1)\left(\frac{0.060 M}{1 M}\right)}=\frac{0.100}{0.060}=\frac{5}{3}=1.7$
2 sig. fig.
$E=-0.0066 \mathrm{~V}$
2 sig. fig.
Answer is not positive. We are not happy.
Time to double check work and, if we find no errors, re-evaluate answer to part (d)!
$\qquad$
13. The following diagram shows the distribution curve for fumaric acid:
[6 marks]

(a) Fumaric acid undergoes two ionizations. What are its pKa values?
[2 marks]

$$
p K_{a 1}=
$$

$\qquad$ 3 $\qquad$ $p K_{a 2}=$ $\qquad$ 4.5 $\qquad$
The $p K_{a}$ value is the $p H$ where the two curves cross. The first one appears to be very slightly higher than 3, so answers like 3.05 or 3.1 would also be accepted. The second one appears to be about halfway between 4 and 5, so answers like 4.4 or 4.6 would also be accepted.
(b) What species are present in solution at $\mathrm{pH}=3.5$ ?
[2 marks]
You do not need to list any species present in lower concentration than $1 \%$.
Your answers must be either chemical formulas or structures. major species:



(c) What species are present in solution at $\mathrm{pH}=5.5$ ?
[2 marks]
You do not need to list any species present in lower concentration than $1 \%$.
Your answers must be either chemical formulas or structures. major species:

minor species:


Name: $\qquad$
14. What is the pH of a 0.27 M aqueous solution of benzoic acid $\left(p K_{a}=4.20\right)$ at $25.00^{\circ} \mathrm{C}$ ? [8 marks]
benzoic acid $=$


|  | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}$ | $\rightleftharpoons$ | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}$ | + |
| :--- | :--- | :--- | :---: | :---: |
| $\mathrm{i}(\mathrm{M})$ | 0.27 | 0 | $\mathrm{H}^{+}$ |  |
| $\mathrm{c}(\mathrm{M})$ | -x |  | +x | $10^{-7}$ |
| $\mathrm{e}(\mathrm{M})$ | $0.27-x \approx 0.27$ | x | +x |  |
|  |  |  | $10^{-7}+x \approx x$ |  |

$K_{a}=\frac{a_{\mathrm{C} 6 \mathrm{H} 5 \mathrm{COO}^{-}} \times a_{\mathrm{H}^{+}}}{a_{\mathrm{C} 6 \mathrm{H} 5 \mathrm{COOH}}}$
$K_{a}=10^{-p K a}=10^{-4.20}=6.3 \times 10^{-5}$
$6.3 \times 10^{-5}=\frac{x \cdot x}{0.27}$
$x^{2}=1.7 \times 10^{-5}$
$x=\sqrt{1.7 \times 10^{-5}}$
$x=\left[H^{+}\right]=0.0041 \mathrm{~mol} / \mathrm{L}$
$p H=-\log (0.0041)=2.38$

If assumption was made, then 1 mark was allotted for checking the assumption:
$0.27 M-0.0041 M=0.27 M$, therefore assumption is valid
If assumption was not made, then 1 mark was allotted for doing the quadratic equation.
15. What was the most interesting and/or useful thing you learned in CHEM 2000?

## DATA SHEET

Some Useful Constants and Formulae

## Fundamental Constants and Conversion Factors

| Atomic mass unit $(\mathrm{u})$ | $1.660539 \times 10^{-27} \mathrm{~kg}$ |  | Kelvin temperature scale | $0 \mathrm{~K}=-273.15{ }^{\circ} \mathrm{C}$ |
| :--- | :--- | :--- | :--- | :--- |
| Avogadro's number $\left(\mathrm{N}_{\mathrm{A}}\right)$ | $6.022141 \times 10^{23} \mathrm{~mol}^{-1}$ |  | $\mathrm{~K}_{\mathrm{w}}\left(\right.$ at $\left.25{ }^{\circ} \mathrm{C}\right)$ | $10^{-14}$ |
| Boltzmann constant $\left(\mathrm{k}_{\mathrm{B}}\right)$ | $1.380649 \times 10^{-23} \mathrm{~J} \cdot \mathrm{~K}^{-1}$ |  | Planck's constant (h) | $6.626070 \times 10^{-34} \mathrm{~J} \cdot \mathrm{~Hz}^{-1}$ |
| Charge of electron | $-1.602176 \times 10^{-19} \mathrm{C}$ |  | Speed of light in vacuum (c) | $2.997925 \mathrm{x} 10^{8} \mathrm{~m} \cdot \mathrm{~s}^{-1}$ |
| Faraday's constant (F) | $96485 \mathrm{C} \cdot \mathrm{mol}^{-1}$ |  | Volume conversion | $1000 \mathrm{~L}=1 \mathrm{~m}$ |
| Ideal gas constant (R) | $8.314462 \mathrm{~J} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}$ | Pressure conversions | $1 \mathrm{bar}=100 \mathrm{kPa}$ |  |
|  | $8.314462 \mathrm{~m}^{3} \cdot{\mathrm{~Pa} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}}$ |  | $1 \mathrm{~atm}=1.01325 \mathrm{bar}$ |  |

## Formulae

$\begin{array}{ll}\bar{K}=\frac{1}{2} m \overline{v^{2}}=\frac{3}{2} R T \quad v_{r m s}=\sqrt{\overline{v^{2}}}=\sqrt{\frac{3 R T}{M}} \quad P V=n R T \\ S=k_{B} \ln \Omega & \Delta S=\frac{q_{r e v}}{T}\end{array} \quad \Delta_{r} G=\Delta_{r} H-T \Delta_{r} S \quad x=\frac{-b \pm \sqrt{b^{2}-4 a c}}{2 a}$

| $\Delta_{\mathrm{r}} \mathrm{G}=\Delta_{\mathrm{r}} \mathrm{G}^{\circ}+\mathrm{RT} \ln \mathrm{Q}$ | $\Delta_{\mathrm{r}} \mathrm{G}^{\circ}=-\mathrm{RT} \ln \mathrm{K}$ | $\ln \left(\frac{K_{2}}{K_{1}}\right)=\frac{\Delta_{r} H^{\circ}}{R}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)$ |
| :--- | :--- | :--- |
| $P_{A}=X_{A} P_{A}^{\circ}$ | $[A]=k_{H} P_{A}$ | $X=\frac{n}{\sum n}$ |

$p H=-\log a_{H^{+}} \quad p K_{a}=-\log K_{a} \quad p K_{b}=-\log K_{b} \quad K_{w}=K_{a} \cdot K_{b} \quad p H=p K_{a}+\log \left(\frac{a_{A^{-}}}{a_{H A}}\right)$
$\Delta H_{r \times n}^{0}=\sum\left(\Delta H_{f}^{0}(\right.$ products $)-\sum\left(\Delta H_{f}^{0}(\right.$ reactants $) \quad \Delta S_{r \times n}^{0}=\sum\left(S^{0}(\right.$ products $)-\sum\left(S^{0}(\right.$ reactants $)$
$\Delta G_{r \times n}^{0}=\sum\left(\Delta G_{f}^{0}(\right.$ products $)-\sum\left(\Delta G_{f}^{0}(\right.$ reactants $)$

## Activities

| Solid | $a=1$ |
| :---: | :---: |
| Pure liquid | $a=1$ |
| Ideal Solvent | $a=X$ |
| Ideal Solute | $a=\frac{c}{c^{\circ}}$ |
| Ideal Gas | $a=\frac{P}{P^{\circ}}$ |



Developed by Prof. R. T. Boeré (updated 2016)

## Some Useful Thermodynamic Properties

| Substance | $\Delta_{f} H^{\circ}\left(\frac{\mathrm{kJ}}{\mathrm{mol}}\right)$ | $\Delta_{f} G^{\circ}\left(\frac{\mathrm{kJ}}{\mathrm{mol}}\right)$ | $S^{\circ}\left(\frac{\mathrm{J}}{\mathrm{mol} \cdot \mathrm{K}}\right)$ |
| :--- | :---: | :---: | :---: |
| $\mathrm{PCl}_{3}(\mathrm{~g})$ | -287 | -268 | 312 |
| $\mathrm{PCl}_{5}(\mathrm{~g})$ | -402 | -323 | 353 |


| Half Reaction | $E^{\circ}(V)$ |
| :---: | :---: |
| $C u_{(a q)}^{2+}+2 e^{-} \rightarrow C u_{(s)}$ | +0.34 |
| $C u_{(a q)}^{2+}+e^{-} \rightarrow C u_{(a q)}^{+}$ | +0.15 |

