# Chem 1A, Fall 2015, Midterm Exam 3. Version A <br> November 17, 2015 <br> (Prof. Head-Gordon) ${ }^{2}$ 

Name: $\qquad$

Student ID: $\qquad$ TA: $\qquad$

Contents: 6 pages
A. Multiple choice (10 points)
B. Thermochemistry and Equilibria (12 points)
C. Chemical and Physical Equilibria (10 points)
D. Second Law and Phases (10 points)
E. Acid and Base Equilibria (12 points)

Total Points: 54 points
Instructions: Closed book exam. Basic scientific calculators are OK. Set brains in high gear and go!
Some possibly useful facts and figures:
$R=8.3145 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \quad$ molar volume at $\mathrm{STP}=22.4 \mathrm{~L} \quad \mathrm{~K}_{\mathrm{w}}=1.0 \times 10^{-14}($ at 25 C$)$
$N_{A v o}=6.0221 \times 10^{23} \mathrm{~mol}^{-1}$
Some possibly relevant equations:

$$
\begin{aligned}
& \Delta U=q+w \quad w_{i r r}=-P_{e x} \Delta V \quad w_{r e v}=-n R T \ln \left(V_{f} / V_{i}\right) \quad q=C \Delta T \quad H=U+P V \\
& \Delta S=\frac{q_{r e v}}{T} \quad \varepsilon=\frac{T_{h}-T_{c}}{T_{h}}=-\frac{w_{\text {net }}}{q_{i n}} \quad \Omega=C V^{N} E^{3 N / 2} \quad S=k \ln \Omega \quad \Delta G=\Delta H-T \Delta S
\end{aligned}
$$

for the reaction $\mathrm{aA}+\mathrm{bB} \leftrightarrow \mathrm{cC}+\mathrm{dD} \quad K=\frac{[\mathrm{C}]_{e q}^{c}[D]_{e q}^{d}}{[A]_{e q}^{a}[B]_{e q}^{b}} \quad Q=\frac{[\mathrm{C}]^{c}[\mathrm{D}]^{d}}{[\mathrm{~A}]^{a}[\mathrm{~B}]^{b}} \quad \Delta G^{o}=-R T \ln K \quad \Delta G=\Delta G^{0}-R T \ln Q$
$\ln K=\frac{-\Delta H^{0}}{R T}+\frac{\Delta S^{0}}{R} \quad \ln \left(\frac{P_{2}}{P_{1}}\right)=-\frac{\Delta H_{\text {vap }}^{\mathrm{o}}}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)$
$\mathrm{pH}=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}_{(\mathrm{aq})}^{+}\right] \quad \mathrm{pK}_{a}=-\log _{10}\left[K_{a}\right] p H=p K_{a}+\log \left(\frac{\left[A^{-}\right]}{[H A]}\right) \quad K_{w}=K_{a} K_{b}$
$P=x_{\text {solvent }} P_{\text {pure }} \quad \Delta T_{\mathrm{b}}=i k_{\mathrm{b}} \times b \quad \Pi=i R T c \quad P_{\mathrm{A}}=x_{\mathrm{A}} P_{\mathrm{A}}^{0}$
A. Multiple choice (10 points): there may be one or more correct solutions, so circle all that apply

1. Circle any of the following that are true about total entropy of the universe
(a) when not at equilibrium, it always increases
(b) when at equilibrium, it attains a maximum value
(c) the change in entropy at equilibrium is zero
(d) it is a state function
2. When the Van't Hoff plot (lnK vs. 1/T) shows a line with a negative slope then
(a) $\Delta \mathrm{H}^{\circ}$ is exothermic
(b) $\Delta \mathrm{H}^{\circ}$ is endothermic
(c) T dependence of $\Delta \mathrm{H}^{\circ}, \Delta \mathrm{S}^{\circ}$ can't be ignored
(d) all of the above
3. Which state function(s) predict spontaneous change under isothermal conditions?
(a) $\Delta \mathrm{G}<0$
(b) $\Delta \mathrm{S}<0$
(c) $\Delta \mathrm{U}<0$
(d) $\Delta \mathrm{H}>0$
4. The hydroxyl ion $\left(\mathrm{OH}^{-}\right)$concentration in pure water at 298 K is
(a) The square root of the ion product, $\mathrm{K}_{\mathrm{w}}$
(b) $10^{-7} \mathrm{M}$
(c) equal to the proton $\mathrm{H}^{+}$concentration
(d) all of the above
5. The quantity $\mathbf{w}=-\mathbf{P} \Delta \mathbf{V}$ describes the work done
(a) expanding against constant external pressure
(b) expanding isothermally
(c) compressing with constant external pressure
(d) heating at constant volume
6. If the enthalpy of a system increases at constant pressure
(a) work was done on the system
(b) work was done by the system
(c) heat was transferred to the system
(d) heat was transferred from the system
7. A heat engine takes in 900 J at high temperature and produces $\mathbf{3 0 0} \mathbf{J}$ of work. What is its efficiency?
(a) $100 \%$
(b) $33 \%$
(c) $50 \%$
(d) $133 \%$
8. An endothermic reaction can be spontaneous if
(a) increase in $T \Delta S$ is greater than decrease in $\Delta H$
(b) when temperature is low
(c) when internal energy is high
(d) at constant pressure
9. Which of the following is a colligative property?
(a) osmotic pressure
(b) boiling point elevation
(c) vapor pressure lowering
(d) all of the above
10. Upon increase in temperature, what will be the ordering of the vapor pressure of the given liquids
(a) propane $<$ hexane $<$ ethanol $<$ water
(b) hexane $<$ propane $<$ water $<$ ethanol
(c) water $<$ ethanol $<$ hexane $<$ propane
(d) none of the above
B. (12 points) Thermochemistry and Equilibria. The Bosch reaction reduces $\mathrm{CO}_{2}$ using hydrogen gas to produce elemental carbon and water vapor. The table on the right provides heats of formation of some of the substances that are relevant to the problem below.

| Substance | $\Delta \mathrm{H}_{\mathrm{f}}^{\circ}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$ |
| :--- | :--- |
| $\mathrm{CO}_{2}$ | -393.51 |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | -285.83 |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ | -241.82 |
| $\mathrm{H}_{2}(\mathrm{~g})$ | 0 |
| $\mathrm{H}(\mathrm{g})$ | 217.96 |

(a) (2 points) Write a balanced equation for this reaction with phases noted.
$\square$
(b) (2 points) Use the provided heats of formation to calculate $\Delta \mathrm{H}^{\circ}(\mathrm{kJ})$ for this reaction.
(c) (2 points) Under what temperature conditions, if any, would this reaction be spontaneous?
(d) (6 points) One way in which spacecraft could regenerate oxygen from the water produced by the Bosch reaction is to convert the water vapor by the water splitting reaction

$$
2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \leftrightarrows 2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})
$$

Give 3 ways to maximize the conversion to products with explanation using Le Chatelier's principle

| How to increase products | Explanation |
| :--- | :--- |
|  |  |
|  |  |
|  |  |
|  |  |

C. (10 points) Chemical and Physical Equilibria. Consider the following reactions:
(i) $4 \mathrm{Na}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \leftrightarrows 2 \mathrm{Na}_{2} \mathrm{O}(\mathrm{s}) \quad \Delta \mathrm{H}=-600 \mathrm{KJ} / \mathrm{mol}$
(ii) $\mathrm{NH}_{4} \mathrm{NO}_{3}(\mathrm{~s}) \leftrightarrows \mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{NO}_{3}^{-}(\mathrm{aq}) \quad \Delta \mathrm{H}=+30 \mathrm{KJ} / \mathrm{mol}$
(iii) sugar(s) $\leftrightarrows \operatorname{sugar}($ soln $) \quad \Delta \mathrm{H}=0 \mathrm{KJ} / \mathrm{mol}$
(iv) $\mathrm{Cl}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) \leftrightarrows 2 \mathrm{HCl}(\mathrm{g}) \quad$ exothermic

Which reactions above correspond to statements given below (there can be more than one correct answer for each sub-question) with brief explanation:
(a) ( 2 point) which of the equilibria will produce more products when heated?

| Reactions | Explanation |
| :--- | :--- |
|  |  |
|  |  |
|  |  |

(b) (2 point) which of the equilibria will produce more products when the pressure is raised?

| Reactions | Explanation |
| :--- | :--- |
|  |  |
|  |  |
|  |  |

(c) (2 point) which of the equilibria will produce more reactants when heated?

| Reactions | Explanation |
| :--- | :--- |
|  |  |
|  |  |
|  |  |

(d) (2 point) which of the equilibria will be unaffected by pressure?

| Reactions | Explanation |
| :--- | :--- |
|  |  |
|  |  |
|  |  |

(e) (2 point) which of the equilibria will be generally unaffected by temperature?

| Reactions | Explanation |
| :--- | :--- |
|  |  |
|  |  |
|  |  |

D. (10 points) Second Law and Phases. The organic compound acetone is a principle ingredient in most nail polish removers. Acetone has a freezing point of $-95.2^{\circ} \mathrm{C}$ and a boiling point of $56.4^{\circ} \mathrm{C}$, and a molar heat of fusion, $\Delta \mathrm{H}_{\text {fus }}=+5.72 \mathrm{~kJ} / \mathrm{mol}$.
(a) (2 point) Calculate the change in entropy, $\Delta \mathrm{S}$, of a sample of acetone at room temperature that absorbs 100J of energy from a blow dryer
$\square$
(b) (2 point) Would $\Delta \mathrm{S}$ be larger or smaller if acetone was at a cold (liquid $\mathrm{N}_{2}$ ) temperature of 77 K ? Explain your answer
(c) (2 point) $\Delta \mathrm{S}^{\circ}{ }_{\text {vap }}$ of acetone is $85 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$. Evaluate the $\Delta \mathrm{H}^{\circ}$ vap and interpret its sign.
(d) (4 point) From the heating curve for acetone and information above:
(i) What temperature is acetone when it is at location B ?
$\square$
(ii) What phase(s) exist between between D and E?

(iii) What is the name of the heat added between D and E and its
 value?


(iv) The temperature of acetone is not changing from B to C, but heat is still being added. Explain.
E. (10 points) Acid and Base Equilibria. Suppose that $0.2 \mathrm{~mol}^{\text {of }} \mathrm{NH}_{3}$ is combined with water to make 1L of solution, and has an equilibrium constant $\mathrm{K}_{\mathrm{b}}=10^{-5}$
(a) (2 point) Write the reaction of ammonia with water
(b) (4 point) Draw up an ICE table that labels columns with reactants and products, describes their initial concentration (I), their change (C) in concentration in terms of unknown $x$, and equilibrium (E) also in terms of $x$

| Reactants/Products $\rightarrow$ |  |  |  |
| :---: | :--- | :--- | :--- |
| $\mathbf{I}$ |  |  |  |
| $\mathbf{C}$ |  |  |  |
| $\mathbf{E}$ |  |  |  |

(c) (2 point) Write down the equation for determining the unknown in $x$ using part (b)
(d) (4 point) Suppose 0.1 mol of the strong acid HCl is added to the solution. Write down an equation for the concentration of $\mathrm{OH}^{-}$(call it y ) after this addition

