# CHEM 1423 <br> Chapter 20 <br> Homework Questions 

## TEXTBOOK HOMEWORK

20.14 Without using Appendix B predict the sign of $\square \mathrm{S}^{\circ}$ for
(a) $\mathrm{CaCO}_{3}(\mathrm{~s})+2 \mathrm{HCl}(\mathrm{aq}) \square \mathrm{CaCl}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{CO}_{2}(\mathrm{~g})$
(b) $2 \mathrm{NO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \square 2 \mathrm{NO}_{2}(\mathrm{~g})$
(c) $2 \mathrm{KClO}_{3}(\mathrm{~s}) \square 2 \mathrm{KCl}(\mathrm{s})+3 \mathrm{O}_{2}(\mathrm{~g})$
20.16 Predict the sign of $\bar{S}$ for each process:
(a) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{g})\left(350 \mathrm{~K}\right.$ and 500 torr) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{g})(350 \mathrm{~K}$ and 250 torr $)$
(b) $\mathrm{N}_{2}(\mathrm{~g})(298 \mathrm{~K}$ and 1 atm$\left.)\right] \mathrm{N}_{2}(\mathrm{aq})$ ( 298 K and 1 atm )
(c) $\mathrm{O}_{2}(\mathrm{aq})(303 \mathrm{~K}$ and 12 atm$) \square \mathrm{O}_{2}(\mathrm{~g})(303 \mathrm{~K}$ and 12 atm$)$
20.21 Without consulting Appendix B, arrange each group in order of increasing molar entropy ( $\mathrm{S}^{\circ}$ ):
(a) Glucose $\left(\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}\right)$, Sucrose $\left(\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}\right)$, Ribose $\left(\mathrm{C}_{5} \mathrm{H}_{10} \mathrm{O}_{5}\right)$
(b) $\mathrm{CaCO}_{3}, \mathrm{Ca}+\mathrm{C}+(3 / 2) \mathrm{O}_{2}, \mathrm{CaO}+\mathrm{CO}_{2}$
(c) $\mathrm{SF}_{6}(\mathrm{~g}), \mathrm{SF}_{4}(\mathrm{~g}), \mathrm{S}_{2} \mathrm{~F}_{10}(\mathrm{~g})$
20.28 For each reaction, predict the sign and find the value of $\square \mathrm{S}^{0}$ :
(a) $3 \mathrm{NO}(\mathrm{g}) \square \mathrm{N}_{2} \mathrm{O}(\mathrm{g})+\mathrm{NO}_{2}(\mathrm{~g})$
(b) $3 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{Fe}_{2} \mathrm{O}_{3}$ (s) $-2 \mathrm{Fe}(\mathrm{s})+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
(c) $\left.\mathrm{P}_{4}(\mathrm{~s})+5 \mathrm{O}_{2}(\mathrm{~g})\right] \mathrm{P}_{4} \mathrm{O}_{10}(\mathrm{~s})$
20.40 Calculate $\square \mathrm{G}^{0}$ for each reaction using $\square \mathrm{G}_{\mathrm{f}}{ }^{0}$ values:
(a) $2 \mathrm{Mg}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \square 2 \mathrm{MgO}(\mathrm{s})$
(b) $\left.2 \mathrm{CH}_{3} \mathrm{OH}(\mathrm{g})+3 \mathrm{O}_{2}(\mathrm{~g})\right] 2 \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
(c) $\left.\mathrm{BaO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g})\right] \mathrm{BaCO}_{3}(\mathrm{~s})$
20.46 One reaction used to produce small quantities of pure $\mathrm{H}_{2}$ is $\left.\mathrm{CH}_{3} \mathrm{OH}(\mathrm{g})\right] \mathrm{CO}(\mathrm{g})+2 \mathrm{H}_{2}(\mathrm{~g})$
(a) Determine $\mathrm{H}^{0}$ and $\mathrm{C} \mathrm{S}^{\circ}$ for the reaction at 298 K
(b) Assuming that these values are relatively independent of temperature, calculate DG 號 $28^{\circ} \mathrm{C}, 128^{\circ} \mathrm{C}$, and $228^{\circ} \mathrm{C}$
(c) What is th significance of thedifferent values of $\left[\mathrm{G}^{\circ}\right.$
20.48 Use $\square \mathrm{H}^{0}$ and $\square \mathrm{S}^{\circ}$ values for the following process at 1 atm to find the normal boiling point of $\mathrm{Br}_{2}: \mathrm{Br}_{2}(\mathrm{l}) \square \mathrm{Br}_{2}(\mathrm{~g})$
20.51 The U.S. government requires automobile fuels to containa renewable component. Fermentation of glucose rom corn yields ethanol, which is added to gasoline to fulfill this requirement.

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\left.\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(\mathrm{~s})\right] 2 \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{l})+2 \mathrm{CO}_{2}(\mathrm{~g})
$$

Calculate $\triangle \mathrm{H}^{\circ}, \square \mathrm{S}^{\circ}$, and $\square \mathrm{G}^{\circ}$ for the reaction at $25^{\circ} \mathrm{C}$. Is the spontaneity of this reaction dependent on T? Explain.
20.56 Calculate K at 298 K for each reaction:
(a) $\mathrm{NO}(\mathrm{g})+(1 / 2) \mathrm{O}_{2}(\mathrm{~g}) \square \mathrm{NO}_{2}(\mathrm{~g})$
(b) $2 \mathrm{HCl}(\mathrm{g})] \mathrm{H}_{2}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})$
(c) 2 C (graphite) $+\mathrm{O}_{2}(\mathrm{~g}) \square 2 \mathrm{CO}(\mathrm{g})$
20.64 The equilibrium constant for the reaction
$\left.2 \mathrm{Fe}^{3+}(\mathrm{aq})+\mathrm{Hg}_{2}{ }^{2+}(\mathrm{aq})\right] 2 \mathrm{Fe}^{2+}(\mathrm{aq})+2 \mathrm{Hg}^{2+}(\mathrm{aq})$ is $\mathrm{K}_{\mathrm{c}}=9.1 \times 10^{-6}$ at 298 K
(a) What is $\mathrm{G}^{\circ}$ at this temperature?
(b) If standard-state concentrations of the reactants and products are mixed, in which direction does the reaction proceed?
(c) Calculate 0 G when $\left[\mathrm{Fe}^{3+}\right]=0.20 \mathrm{M},\left[\mathrm{Hg}_{2}{ }^{2+}\right]=0.010 \mathrm{M}$, $\left[\mathrm{Fe}^{2+}\right]=0.010 \mathrm{M}$, and $\left[\mathrm{Hg}^{2+}\right]=0.025 \mathrm{M}$.
In which direction will the reaction proceed to achiece equillibrium?
20.74 (a) Write a balanced equation for the gaseous reaction between $\mathrm{N}_{2} \mathrm{O}_{5}$ and $\mathrm{F}_{2}$ to form $\mathrm{NF}_{3}$ and $\mathrm{O}_{2}$.
(b) Determine $\mathrm{GG}^{\circ}{ }_{\mathrm{rxn}}$
(c) Find $\mathrm{G}_{\mathrm{rxn}}$ at 298 K if $\mathrm{P}_{\mathrm{N} 2 \mathrm{O} 5}=\mathrm{P}_{\mathrm{F} 2}=0.20 \mathrm{M}, \mathrm{P}_{\mathrm{NF} 3}=0.25 \mathrm{~atm}$ and $\mathrm{P}_{\mathrm{O} 2}=0.50 \mathrm{~atm}$

## SUPPLEMENTARY HOMEWORK

S1. If a reaction is spontaneous at any temperature, then $\Delta \mathrm{H}^{\mathrm{O}}$ is $\qquad$ and $\Delta S^{\circ}$ is
a. positive; positive
b. positive; negative
c. zero; positive
d. negative; positive
e. negative; negative

S2. At constant $T$ and $P$, in which of the following situations will the reaction never be spontaneous?
a. $\Delta H>0$ and $\Delta S<0$
b. $\Delta H>0$ and $\Delta S>0$
c. $\Delta H<0$ and $\Delta S<0$
d. $\Delta H<0$ and $\Delta S>0$
e. none of the above

S3. A reaction is exothermic and has a negative value of $\Delta S^{0}$. The value of $\Delta \mathrm{G}^{0}$ for this reaction is therefore:
a. negative at all temperatures.
b. positive at all temperatures.
c. positive above $0^{\circ} \mathrm{C}$ and negative below $0^{\circ} \mathrm{C}$.
d. positive above a certain temperature and negative below it.
e. negative above a certain temperature and positive below it.

S4. The reaction $\mathrm{A} \rightarrow \mathrm{B}$ is exergonic at $25^{\circ} \mathrm{C}$ and the enthalpy change is +20 kJ . What can be concluded about the entropy change for this reaction?
a. $\Delta \mathrm{S}>+67 \mathrm{~J} / \mathrm{K}$
b. $\Delta \mathrm{S}>+800 \mathrm{~J} / \mathrm{K}$
c. $\Delta \mathrm{S}<-67 \mathrm{~J} / \mathrm{K}$
d. No conclusion can be made about $\Delta \mathrm{S}$

S5. For the endergonic reaction $C \rightarrow D, \Delta S=+20 \mathrm{~J} / \mathrm{K}$. For this reaction,
a. $\Delta \mathrm{G}<0 \& \Delta \mathrm{H}<0$
b. $\Delta \mathrm{G}>0$ \& $\Delta \mathrm{H}<0$
c. $\Delta \mathrm{G}<0 \& \Delta \mathrm{H}>0$
d. $\Delta \mathrm{G}>0 \& \Delta \mathrm{H}>0$

S6. Consider a sample containing 322 grams of toluene $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{3}, \mathrm{M}=92\right)$.

| Quantity | $\mathrm{T}_{\mathrm{m}}$ | $\mathrm{T}_{\mathrm{b}}$ | $\square \mathrm{H}_{\text {us }}{ }^{\circ}$ | $\square \mathrm{H}_{\text {sap }}{ }^{\mathrm{o}}$ | $\square \mathrm{S}_{\text {us }}{ }^{\circ}$ | $\square \mathrm{S}_{\text {ap }}{ }^{\mathrm{o}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Value | -95 | +111 | 6.64 | 38.1 | 37.3 | $99.2 \mathrm{~J} / \mathrm{mol}-$ |
|  | ${ }^{\circ} \mathrm{C}$ | ${ }^{\circ} \mathrm{C}$ | $\mathrm{kJ} / \mathrm{mol}$ | $\mathrm{kJ} / \mathrm{mol}$ | $\mathrm{J} / \mathrm{mol}-\mathrm{K}$ | K |

(a) Calculate $\square \mathrm{S}_{\text {sys }}, \bar{\square} \mathrm{S}_{\text {surr }}$ and $\square \mathrm{S}_{\text {univ }}$ for the vaporization of 322 grams of toluene at:
(1) $130{ }^{\circ} \mathrm{C}$, (2) $111{ }^{\circ} \mathrm{C}$, (3) $90^{\circ} \mathrm{C}$
(b) Calculate $\square \mathrm{G}^{\circ}$ for the vaporization of 322 grams of toluene at:
(1) $130^{\circ} \mathrm{C}$, (2) $111{ }^{\circ} \mathrm{C}$, (3) $90^{\circ} \mathrm{C}$
(c) Calculate $\square \mathrm{S}_{\text {sys }}, \square \mathrm{S}_{\text {surr }}$ and $\square \mathrm{S}_{\text {univ }}$ for the freezing (crystallization) of 322 grams of toluene at:
(1) $-115{ }^{\circ} \mathrm{C},(2)-95^{\circ} \mathrm{C},(3)-75^{\circ} \mathrm{C}$
(d) Calculate $\mathrm{G}^{\circ}$ for the freezing (crystallization) of 322 grams of toluene at: (1) $-115{ }^{\circ} \mathrm{C},(2)-95{ }^{\circ} \mathrm{C},(3)-75{ }^{\circ} \mathrm{C}$

S7. A certain reaction has $\Delta \mathrm{H}^{\circ}=+177.8 \mathrm{~kJ}$, and $\Delta \mathrm{S}^{\circ}=+160.5 \mathrm{~J} / \mathrm{K}$. Above or below what temperature (in ${ }^{\circ} \mathrm{C}$ ) does it become spontaneous ?

S8. For the reaction shown, $\Delta \mathrm{G}^{\circ}=-32.8 \mathrm{~kJ}$ at $25^{\circ} \mathrm{C}$.

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\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

a. Calculate the equilibrium constant for this reaction at $250^{\circ} \mathrm{C}$.
b. Is a mixture of the three gases where $\mathrm{pN}_{2}=3.5$ bar, $\mathrm{pH}_{2}=1.2$ bar, and $\mathrm{pNH}_{3}$
$=0.22$ bar at equilibrium? Justify your answer.
c. What is the value of $\Delta \mathrm{G}$ under the conditions of part b?

S9. For the reaction, $\mathrm{CaCO}_{3}(\mathrm{~s}) \rightarrow \mathrm{CaO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g}), \Delta \mathrm{H}^{0}=+178 \mathrm{~kJ} / \mathrm{mol}$ and $\Delta \mathrm{S}^{0}=$ +161 J/mol-K.
a. What is the value of $\Delta \mathrm{G}^{\mathrm{o}}$ at $25^{\circ} \mathrm{C}$ ?
b. What is the value of $\Delta \mathrm{G}^{\circ}$ at $1500^{\circ} \mathrm{C}$ ?
c. At what temperature, in ${ }^{\circ} \mathrm{C}$, are the reactants and products in equilibrium? (i.e. $\Delta G^{0}=0$ )

S10. A hypothetical polypeptide, PP , has two structural forms, $\operatorname{PP}(\alpha)$ and $\operatorname{PP}(\beta)$. For the transition, $\operatorname{PP}(\alpha) \rightarrow \operatorname{PP}(\beta)$, the entropy change is $-120 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$ and the enthalpy change is $-42 \mathrm{~kJ} / \mathrm{mol}$.
This transition is spontaneous $\qquad$ (above or below) $\qquad$ ${ }^{\circ} \mathrm{C}$.

